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Activated Carbon Process for the Treatment of Cadmium(II) Containing Wastewaters

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In the batch mode experiments, the effects of pH, carbon to Cd(II) ratio, temperature, ionic strength and mixing rate were studied. A suspension-polymerization technique was used to prepare activated carbon beads from one powdered carbon. The Cd(II) adsorption characteristics of the activated carbon beads were compared with the original powdered carbon.

Chemical regeneration with strong acid of the exhausted carbon was examined, along with thermal-chemical process.

Two Cd(II) treatment schemes were proposed, together with an economic evaluation of each scheme. The cost of the activated carbon adsorption process was also compared with several treatment processes including insoluble sulfide precipitation, alkaline neutralization precipitation, and ion exchange process.

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ACTIVATED CARBON PROCESS FOR THE TREATMENT OF CADMIUM(II) - CONTAINING WASTEWATERS

by

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FOREWORD

When energy and material resources are extracted, processed, converted, and used, the related pollutional impacts on our environment and even on our health often require that new and increasingly more efficient pollution control methods be used. The Industrial Environmental Research Laboratory - Cincinnati (IERL-CI) assists in developing and demonstrating new and improved methodologies that will meet these needs both efficiently and economically.

This report is a product of the above efforts. These studies were undertaken to perform a laboratory-scale development of an activated carbon process for treatment of cadmium (II) - containing wastewaters. Various factors that may affect the cadmium (II) removal efficiency in addition to various chemical regeneration methods were thoroughly studied.

Such information will be of value both to EPA's regulatory program (Effluent Guideline Division) and to the industry itself in arriving at meaningful and achievable discharge levels. Within EPA's R & D program the information will be used as part of the continuing program to develop and evaluate improved and less costly technology to minimize industrial waste discharges. This technology may find application in treatment of metal-containing wastes generated by many industries.

For further information concerning this project the Industrial Pollution Control Division should be contacted.

David G. Stephan
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ABSTRACT

The removal of Cd(II) from two synthetic cadmium-containing wastewaters by an activated carbon adsorption process has been investigated. Among the 17 different types of activated carbon tested, it was found that the acidic activated carbons, namely Nuchar SA and Nuchar SN exhibited the greatest Cd(II) removal capacity.

In the batch mode experiments, the effects of pH, carbon to Cd(II) ratio, temperature, ionic strength and mixing rate were studied. A suspension-polymerization technique was used to prepare activated carbon beads from one powdered carbon. The Cd(II) adsorption characteristics of the activated carbon beads were compared with the original powdered carbon. Chemical regeneration with strong acid of the exhausted carbon was examined, along with thermal-chemical process.

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SECTION 1

INTRODUCTION

The presence of cadmium in the environment has led to an increasing awareness and concern of its detrimental effect to nature and human health. The effects of trace amounts of cadmium on human health are well-documented (1).

Cadmium is a non-essential and non-beneficial element to both plants and animals. Its compounds have been shown to affect many organs and body systems. There is evidence from tests on man, as well as on some lower animals, that cadmium ingestion can have adverse effects on vascular function, on blood tissue and blood elements, on male and female reproductive organs, on the liver, on bones, and probably most significantly, on renal function (2,3).

In connection with vascular effects, Perry and Schroeder (4) have presented evidence of increased excretion of cadmium in the urine of hypertensive people, which could suggest that cadmium absorption by the body can cause hypertension. In his tests, Schroeder (5) attempted to duplicate the human condition of chronic hypertensive disease in the laboratory with rats. The animals were given trace amounts of cadmium (5 ppm) in their drinking water from the time of their weaning. Cadmium produced hypertension in the rats after approximately one year and the effect increased with age. The life spans of the rats were also shortened. Additional tests by Schroeder, et al. (6) involving cadmium and zinc concentrations in the kidneys of both hypertensive and normotensive rats, suggested a correlation between the renal Cd/Zn ratio and the level of blood pressure. In these tests, a renal Cd/Zn ratio of greater than 0.80 indicated hypertension. The author concluded, on the basis of his data, that cadmium might be a factor in hypertension of unknown origin in humans, due to its ability to inhibit the utilization of zinc (6).

With regard to blood effects, Decker et al. (7) studied the impact of ingestion of low levels of cadmium (0.1 to 50 ppm) on young rats. The animals were all sacrificed at various intervals up to one year. Upon analysis of blood and tissue samples of the rats, they found a 50 percent reduction in hemoglobin in those ingesting 50 ppm cadmium for three months. There was no significant reduction in those administered from 0.1 to 10 ppm cadmium. In a study involving workers exposed to cadmium dust and fumes, Piscator et al. (8) found a significant correlation between high cadmium and low hemoglobin concentrations in blood.

In one of many research efforts to determine the effects of cadmium on reproductive organs, Nordberg (9) found that single subcutaneous injections of cadmium, at 1 mg-Cd/ℓ, caused complete testicular necrosis in mice. In

another study, metabolism in the testis was found to change due to an increase in testicular temperature after intravenous administration of cadmium (10). Studies such as these stimulated research on the effects of cadmium on ovaries. For example, Kar et al. (11) reported acute changes in the ovaries of prepubertal rats following subcutaneous injection of cadmium chloride at 10 mg-Cd/ℓ.

In a 1976 bulletin, the National Institute for Occupational Safety and Health (NIOSH) (12), reported that in a study by Friberg, ingestion by rabbits resulted in liver damage terminating in cirrhosis. Another investigation by Prodan, this one involving cats, revealed fatty infiltration of livers due to cadmium administration (12). There have also been several reports concerning changes in liver function in humans exposed to cadmium, but the results have been conflicting and additional studies are needed before any definite conclusions can be reached.

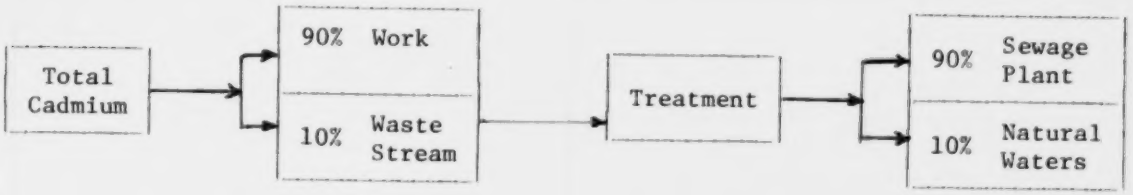
Perhaps the most notorious episode of cadmium poisoning was the outbreak of the Itai-Itai ("ouch-ouch") disease which occurred in Japan from the late forties to the sixties. The disease is actually osteomalacia, a skeletal disorder characterized by painful joints and bones, particularly in the back and legs. The problem in this case was attributed to pollution of water and crops by cadmium-containing wastewater from copper-, lead-, and zinc-sulfide mining and smelting works (8,13).

There is a large volume of evidence relating the ingestion of cadmium to changes in kidney function. This evidence is normally presented in terms of urinary excretion of a low molecular weight protein (2,14). In other cases, renal dysfunction has been observed as glucosuria (1,14), reduced urine-concentration ability, various changes in the processing of calcium and phosphorus by the kidneys (1), and the occasional formation of kidney stones (2). These disorders come about as accumulated cadmium in kidneys exchanges with zinc in the enzymes necessary for readsorption and catabolism of proteins. Thus, less protein is catabolized or readsorbed and tubular proteinuria results (8).

In addition to the problems already mentioned, there is evidence indicating that exposure to cadmium through inhalation can produce effects on the respiratory and nervous systems. There is also evidence to suggest that cadmium may cause cancer and birth deformities. Perhaps the major concern with respect to cadmium toxicity is that it has a long biological half-life in man, estimated at 10 to 25 years (13). In short, cadmium is a serious threat to human health. Browning (3) quoted Christensen and Olsen as saying that, "Cadmium has probably more lethal possibilities than any of the other metals." Friberg (8) added: "All such long half-life substances should be controlled to the greatest extent possible."

Furthermore, it is also known that cadmium is not readily degradable in the environment, its contamination potential therefore increases considerably as greater quantities of cadmium are refined and used. United States consumption of cadmium from 1961 to 1970 was at an average of 5.3 million kg per year, with a high of 6.9 million kg in 1969. This is a 20 percent increase over the average yearly consumption of 4.4 million kg during the previous decade, from 1951 to 1960 (15). World-wide production of cadmium in 1970 was reported to

be almost 16 million kg (16). By far the greatest single user of cadmium was the electroplating industry (45%). The metal imparts an attractive corrosion resistant finish to ferrous metals. The amount of cadmium resulting in water pollution from plating establishments is not known exactly but an estimate has been made. Studies conducted by Yost (17) has led to the following description of cadmium flow from the plating industry:



Based on this estimate, during 1968, 273,000 kg (or 600,000 lb) of cadmium was discharged into waste streams prior to treatment. Assuming a treatment efficiency of 90% for cadmium removal, 27,300 kg (or 60,000 lb) of cadmium found its way into either treatment plants or natural waters. This is a sizeable amount of cadmium being discharged into the environment. In order to control this source of pollution, better treatment techniques must be employed.

The removal of heavy metals, including cadmium, from wastewater has become a subject of intense interest since 1970. A large volume of research has been undertaken to investigate the various possible removal techniques. Much of this recent work has been conducted by foreign scientists, in particular the Russians and Japanese. Some of their work, plus that of several others is reviewed by Smith (18). There are, of course, many physical, chemical, and economic aspects to be considered in selecting the "best" treatment scheme for a particular wastewater, with "best" being defined here as that process which provides the necessary or desired removal of the pollutant at the lowest possible cost.

Although precipitation is the method employed most often in current heavy metal treatment, this method has some definite drawbacks. The main disadvantage is that the precipitated metal solids must be coagulated, thickened, and further concentrated. Also, the disposal and treatment of chemical sludges such as $Cd(OH)_2(s)$, $CdCO_3(s)$, and $CdS(s)$ remains largely unexplored. Furthermore, the presence of organic and inorganic complex forming ligands in wastewater almost always renders processes such as chemical precipitation and ion exchange ineffective, but may actually enhance metal adsorption (19).

According to Huang and Ostovic (19) and Huang and Smith (20), the activated carbon adsorption process has definite potential for the treatment of heavy metal wastewaters in general, and cadmium wastewaters in particular. Activated carbon can be easily manufactured from any of a host of carbonaceous materials, including wood, coconut shells, anthracite coal, and petroleum coke. Spent carbon can be regenerated for reuse, an attractive economic feature. Its high specific surface area makes it an ideal adsorbent, provided that the adsorbate has an affinity for the carbon surface. Since activated carbon is manufactured from so many different starting materials using various

activation processes, there is a seemingly infinite number of unique brands, each with its own particular surface and chemical properties. Several extensive attempts have been made with the hope of characterizing the surface functional groups of this material (21,22,23,24). Yet, in spite of these efforts, surprisingly little is actually known about the exact nature of the surface chemistry of activated carbons. This void is due not only to difficulties in experimental methods, but also to difficulties in establishing comparable trends among such a variety of materials.

From an application standpoint, however, the availability of such a wide range of substances means that there is an excellent chance of finding a suitable adsorbent for almost any pollutant. Results from an investigation by Huang and Ostovic (19) and Smith and Huang (20) demonstrated that cadmium can be appreciably adsorbed from aqueous solution by activated carbon. It is therefore the aim of this research to investigate the treatability of cadmium-containing industrial wastewater, exemplified by cadmium plating wastewater, by activated carbon adsorption. Factors that may affect the removal of cadmium (II) ion from wastewater were thoroughly studied. Finally, treatment schemes suitable for cadmium-containing industrial wastewater were proposed with economical analysis for comparison with other common cadmium treatment processes.

SECTION 2

CONCLUSIONS

Among the 17 different brands of commercial activated carbon tested, the acidic types such as Nuchar SA and Nuchar SN are the most effective adsorbents for Cd(II) removal. These are powdered activated carbons and have a relatively low pH_{zpc}.

The extent of Cd(II) removal depends significantly on the pH value. For all types of activated carbon examined, the extent of Cd(II) removal from the cadmium fluoroborate solution increases with increasing pH, reaches a plateau then remains constant, presumably due to chemical precipitation. The extent of Cd(II) removal from the cadmium cyanide solution, however, peaks at pH 6. The presence of cyanide at concentrations greater than the cadmium (II) tends to inhibit Cd(II) removal by activated carbon adsorption. Cadmium removal by chemical precipitation can be totally inhibited by cyanide.

Other factors such as carbon to cadmium ratio, ionic strength, and temperature can also affect the extent of cadmium (II) removal. A critical carbon to cadmium (mass) ratio is required for maximum cadmium (II) removal. The extent of cadmium (II) removal decreases with increasing ionic strength. The increase in temperature tends to slightly increase the extent of cadmium removal.

The kinetics of cadmium adsorption from both the cyanide and fluoroborate plating wastewater are quite simple; the reaction proceeds very fast, almost reaching the maximum level within the first few minutes of contact time. Varying parameters such as pH, carbon dose, ionic strength, and temperature do not change the rate of removal. Carbon type, i.e., powdered or granular, appears to be the most influencing variable; powdered carbons attain equilibrium adsorption more rapidly than granular brands.

Since proton ions compete favorably with cadmium ions, particularly at the low pH region, the spent carbon can be readily regenerated by strong acids such as sulfuric, hydrochloric and perchloric acids at ambient temperature. The acid regeneration reaction takes place moderately fast.

Pretreatment of the basic activated carbons such as Filtrasorb 400 that has a pH_{zpc} of 7 by sodium methylate and carbon disulfide failed to improve the cadmium removal capacity.

With the use of a suspension-polymerization technique, it is possible to make activated carbon beads from the originally powdered activated carbon.

The beads contain 70% by weight of activated carbon. The Cd(II) adsorption capacity of the activated carbon beads is essentially the same as the originally powdered activated carbon. However, due to intraparticle diffusional resistance, the rate of Cd(II) adsorption on carbon beads is slower than that of the original carbon. The rate of Cd(II) removal by the activated carbon beads can be described by the equation

$$\frac{d[Cd(II)]_{ads}}{dt} = k[Cd(II)][C](1-\Theta)$$

where [Cd(II)] is the temporal cadmium concentration in mole/ℓ; [C] is the temporal carbon concentration in gm/ℓ; Θ is the fraction of surface coverage; and t is the reaction time in minutes.

The cost of activated carbon adsorption process is favorably comparable with other major treatment schemes such as insoluble sulfide precipitation and ion exchange process. The operational and maintenance cost constitutes a large portion of total cost and the cost of activated carbon appears to be an important contributing factor to it.

SECTION 3

RECOMMENDATIONS

In this study, the parameters affecting the extent of cadmium (II) removal from synthetic plating wastewaters were thoroughly examined. An actual wastewater will generally adhere to all of the theories, equations and treatment trends established in this report.

The chemical composition of actual wastewater may differ significantly from the laboratory prepared wastewater. These differences in solution chemistry may alter the rate and the extent of Cd(II) removal for an actual wastewater. Therefore, a separate evaluation of each individual case is necessary.

The following procedures are recommended for designing full-scale activated carbon treatment process:

1. Obtain a typical sample of the wastewater to be treated (ca 50 gallons).

2. Perform several batch laboratory experiments at various adjusted solution pH's (one-liter samples with 2 grams carbon at initial pH 6 to 8 are recommended).

3. Adjust the wastewater to the desired pH value and run several laboratory scale packed columns with different depth of carbon in each (at least three different depths) until breakthrough. The carbon should be prewashed with clean water at the same pH as the adjusted wastewater. A flow rate of 2 gal/min-ft^2 is recommended.

4. Exhausted carbon should be regenerated in batch experiments with various strengths of acidic solution to determine the time and the volume needed for regeneration. At least 10 grams of exhausted carbon per 200 mℓ of acidic solution should be used.

The experimental data obtained from the procedures outlined above can be evaluated and used to determine the following design parameters:

a. the rate of Cd(II) adsorption
b. the Cd(II) adsorption capacity
c. the amount of carbon needed

d. the frequency of carbon regeneration
e. the volume of acid regenerant solution needed
f. the cost of operating the system.

To improve this effort and establish a more complete set of criteria for operating an activated carbon system to remove Cd(II) from solution the following are recommended:

1. A full-scale system should be established in a small plant and operational parameters applied.

2. More studies are needed to obtain operational parameters on the production of activated carbon beads at mass quantity.

3. Further work should be done to study the separation of powdered activated carbon from solution.

4. More experimental work must be done on the effect of coagulation agents such as polymers and alum on the Cd(II) adsorption characteristics of the powdered activated carbon.

SECTION 4

BACKGROUND INFORMATION

CADMIUM PLATING WASTEWATERS

Cadmium plating first attracted industrial interest between 1914 and 1919 when Udy patented an electroplating process from the cyanide bath (25). Today there are several hundred cadmium plating establishments in the United States, with the major concentration of plants being located in the Midwest, Northeast, and along the Western seaboard (26). Some of the major industries that use cadmium plating are the automotive industry; appliance manufacturers; the radio, television, and electronics industry; and manufacturers of metal fasteners (26).

Electroplating imparts several desirable physical properties onto metal parts, some of which include conductivity, corrosion resistance, durability, and decoration (26). Cadmium plating in particular is preferred for application to tropic or marine atmospheres (25). It is used extensively on iron and steel parts because of its anodic relationship to iron. Thus, even if the cadmium becomes nicked or scratched, exposing the base metal, the ferrous metal remains protected. Cadmium plating is also popular because of its ability to reduce galvanic corrosion, occurring when two dissimilar metals are assembled together (26). Cadmium plating should not be used in cases where the exposure to other chemicals is high or in the plating of metal food containers due to the potential for cadmium poisoning of the contents.

By far, the greatest amount of cadmium plating is done in the cyanide bath (27). The next most common is the fluoborate bath, followed by more specialized plating solutions made up from cadmium salts such as sulfamate, sulfate, and acetate (25).

The cyanide bath is popular for cadmium plating because of its high throwing power, i.e., smoothness in deposition. It is extremely poisonous and care must be taken in plating shops to avoid excessive evolution of cadmium and cyanide vapors. The cyanide bath has a rather low cathode current efficiency and, as a result, problems with hydrogen embrittlement have been encountered in the cadmium plating of certain high-strength steels (25). This, in fact, has led to the development of some of the other plating solutions for cadmium. Cadmium fluoborate baths are not poisonous, very stable, and easily controlled. They have much less throwing power than cyanide baths, but they have the advantage of plating at very high current densities with almost 100 percent current efficiency and no hydrogen embrittlement. The cadmium fluoborate bath is applied chiefly in barrel plating of cast or malle-

able iron parts, as well as in strip and wire plating (27). Table 1 gives the typical make-up of both a cyanide and a fluoborate bath for cadmium plating.

TABLE 1. Typical Make-Up of Cadmium Electroplating Baths (25,27,28).

Cadmium Cyanide Bath		Cadmium Fluoborate Bath	
Cadmium Oxide	22.47- 41.19 g/ℓ	Cadmium Fluoborate	241.15 g/ℓ
(Cadmium as metal)	19.47- 35.95 g/ℓ	(Cadmium as metal)	94.36 g/ℓ
Sodium Cyanide	77.89-161.77 g/ℓ	Ammonium Fluoborate	59.91 g/ℓ
Temperature	24 - 32°C	Boric Acid	26.96 g/ℓ
		Temperature	21 - 38°C
		pH	3 - 3.5

Figure 1 gives a typical cadmium plating process for iron and steel parts, as well as one for aluminum and aluminum alloys. Each step in the process is a potential contributor of toxic wastes to the wastewater flow. The various

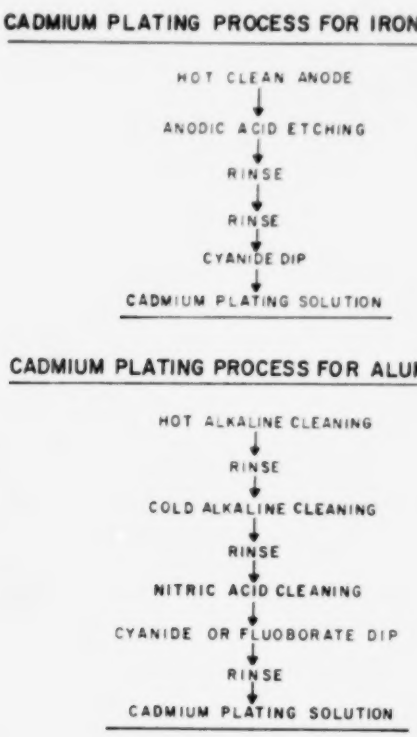


Figure 1. Common steps in cadmium plating operation (29).

acid dips, etches, and alkaline cleaning processes are designed mainly to remove oils, grease, surface stains, oxide films or any other substances which might serve as a barrier between the deposited metal coating and the base metal being plated. Such substances could cause unevenly formed or loosely adhering deposits (29).

Alkaline cleaners, as in the cadmium plating process for aluminum, consist of mixtures of alkaline salts and surfactants to emulsify oils and grease and to disperse soils on the metal parts to be plated (29). In general, these solutions do not accumulate appreciable amounts of toxic wastes. Acid dips consist of hydrochloric, sulfuric, hydrofluoric, or nitric acids, or mixtures of these. They do not normally contain high concentrations of toxic metals, with one exception. In hydrochloric acid dips employed in barrel plating operations, the dissolution of cadmium, zinc, or chromium from the metal contacts can produce rather high contamination levels. Occasionally, these acid dips are also used as chemical stripping solutions for cadmium and zinc, and in such cases they can contain up to 25,000 ppm of dissolved metal (29).

As indicated by the charts in Figure 1, each step in the cleaning process is followed by rinsing. This produces a large volume of effluent, usually containing only trace amounts of metal. Another waste producing operation is the periodic discarding of expended process solutions due to the accumulation of grease, oil, dirt, and metallic impurities (30). This is periodically essential since such impurities can have an adverse effect on the quality of the cadmium plate. For example, in a cadmium cyanide bath, the accumulation of calcium or magnesium can bring about harmful precipitates in the bath, while traces of iron would cause the cadmium plate to be hazy in appearance. In a cadmium fluoborate bath, the presence of chloride would cause the cadmium deposits to be very rough, and certain organics would promote streakiness and bad color of deposits (31). Finally, accidental overflows from the plating solutions and dripping from work in progress between the various process solutions and rinse tanks serve as sources of cadmium contamination in the wastewater (30).

Table 2 gives concentration levels of various substances for several cadmium plating wastewater effluents. From this it can be seen that a typical cadmium plating wastewater contains 7 to 15 mg-Cd/ℓ (or about 1×10^{-4} M), but some installations have reported as much as 50 mg-Cd/ℓ (or 4.5×10^{-4} M) in the wastewater stream.

As evidenced by toxicity studies, cadmium concentrations at these levels present a definite hazard to the aquatic environment. Therefore, it becomes necessary to design alternatives that will reduce the cadmium pollution problem due to electroplating. One suggested alternative is to find another substance to replace cadmium in the plating process. However, the substitution potential for cadmium is really quite limited. Zinc is the only practical substitute, since the two metals have some similar properties and are both used extensively in electroplating. Yet there are also some distinct differences that render cadmium superior in certain applications. For example, cadmium reduces corrosion more than zinc, an important fact with respect to current flow in electrical components. Also, a cadmium finish retains its initial appearance longer and, as mentioned earlier, is more effective in

preventing galvanic corrosion than zinc. Another major difference is that zinc cannot be soldered, whereas cadmium actually increases the ability of a metal to be soldered and must therefore be used where solderability is necessary. The environment to which a metal part is to be exposed also plays a key role in the selection of a suitable plating metal. For instance, zinc is superior to cadmium in an industrial environment, but cadmium will provide better protection in marine atmospheres. Both will give the same relative protection in rural areas. In terms of cost, a cadmium metal anode is about thirteen times as expensive as a zinc anode. However, this has little bearing on the selection since the cost of plating material is merely a small portion of the total plating cost. Also, most metal finishing costs are usually a small percentage (less than 5 percent) of the final cost of the product. Therefore, substitution appears to have low potential due to both the lack of economic incentive and the specialized cases for which cadmium plating is necessary.

TABLE 2. Reported Concentrations in Cadmium Plating Wastewaters (29,32,33).

Process	Concentration (mg/ℓ)
Automobile heating control manufacturing - Cd plating	Cd = 14 - 22
Plating rinse waters (large installations)	Cd = 15 (avg); 50 (max)
Automatic barrel zinc and cadmium plating plant:	
Alkalinity (as Na_2O)	70 - 95
Hydrochloric acid (HCl)	160 - 200
Nitric acid (HNO_3)	0 - 10
Chromates (as Cr)	2 - 25
Zinc (as Zn)	20 - 30
Cadmium (as Cd)	10 - 15
Mixed manually operated barrel and rack plating plant:	
Alkalinity (as Na_2O)	80 - 100
Hydrochloric acid (HCl)	140 - 190
Sulfuric acid (H_2SO_4)	420 - 470
Nitric acid (HNO_3)	140 - 190
Phosphoric acid (H_3PO_4)	200 - 270
Cyanide (as CN)	40 - 50
Cadmium (as Cd)	7 - 12
Chromate (as Cr)	15 - 25
Copper (as Cu)	3 - 8
Nickel (as Ni)	15 - 25
Zinc (as Zn)	5 - 10

Another obvious alternative in eliminating cadmium from wastewater due to electroplating would be for plating firms to no longer offer cadmium plating. This is exactly what has happened in the city of Philadelphia,

where nearly all of the cadmium plating firms have discontinued their cadmium processes. The Philadelphia Water Department's "Wastewater Control Regulations," which became effective on January 1, 1977, called for a cadmium limit of 0.1 ppm in the wastewater to be achieved by July 1, 1977. The regulation was deemed necessary due to the large cadmium loadings to the city's water treatment plants, particularly the Northeast facility, where cadmium loadings of almost 7 kg (dry wt) per day could be attributed to cadmium plating operations. Rather than initiate plans and build facilities to treat their cadmium wastes, all but 4 of the city's 44 cadmium plating establishments stopped offering cadmium plating by the July 1, 1977 deadline, with 2 of the remaining 4 choosing to end operations at a later date. Of the 2 remaining firms, one has made plating bath and rinse flow modifications to bring their effluent into compliance with the 0.1 ppm limit, while the other plant has made a commitment to develop a chemical treatment system for its cadmium wastewaters (18).

There are several socio-economic factors to be considered in evaluating the various alternatives available for the solution of a particular cadmium pollution problem. Yet in view of the advantages of the specialized uses of cadmium plating, the development and implementation of an effective and economical process for the treatment of cadmium containing wastewater would certainly be a more progressive approach than to discontinue cadmium plating altogether.

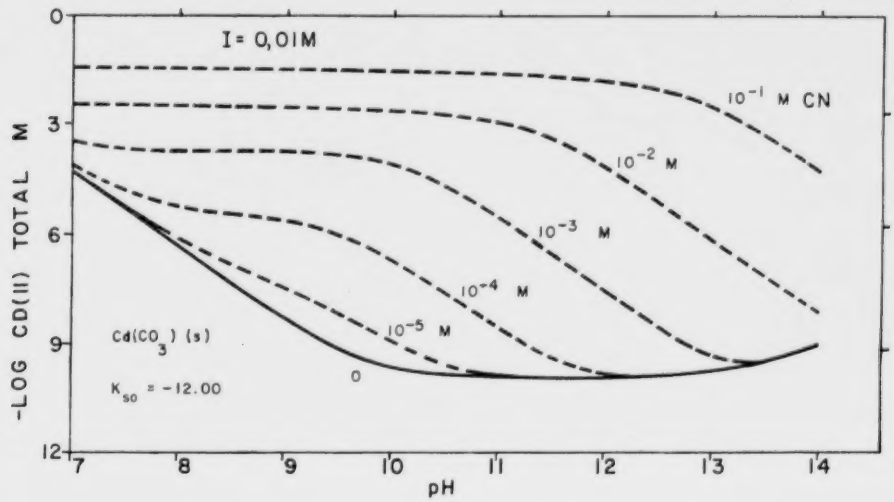
AQUEOUS CHEMISTRY OF CADMIUM IN RELATION TO PLATING WASTEWATERS

Metal solubility, complexation with coexisting ligands, and precipitation are important factors to be considered in seeking to understand the adsorption of metal ions from solution. For example, complexation can alter the solubility, charge characteristics, or size of a metal ion, thus changing its adsorptive character. This work attempts to model two plating wastewater solutions (cadmium fluoborate and cadmium cyanide), and examine the adsorptive behavior of cadmium onto activated carbon from these two different systems.

The solubility of cadmium in aqueous solutions is usually governed by cadmium carbonate and cadmium hydroxide. In the presence of complex forming agents, such as CN^-, the solubility of cadmium may increase. Figures 2 and 3 demonstrate this phenomenon.

The solid line in Figure 2 is the solubility of $CdCO_3(s)$ in the absence of ligand. The dashed lines depict the solubility in the presence of various concentrations of cyanide. Figure 3 is a similar plot for the solubility of $Cd(OH)_2(s)$ in aqueous solution. It is obvious that the presence of cyanide substantially increases the solubility of cadmium for these two systems. This is due to the fact that cyanide forms several stable complexes with cadmium, namely $Cd(CN)^+$, $Cd(CN)_2$, $Cd(CN)_3^-$, and $Cd(CN)_4^{-2}$. For a cadmium plating bath in which cyanide is used as the electrolyte, the composition of the cadmium-cyanide complex is not unequivocally known. Lowenheim (29) reports that the complex of greatest importance is $Cd(CN)_4^{-2}$. Raub and Muller, on the other hand, suggest that cadmium is deposited from either $Cd(CN)_2$ or $Cd(CN)_3^-$, depending on the free cyanide concentration in the

bath (34). These complexes, and their distribution as a function of pH, are also shown in Figures 2 and 3.



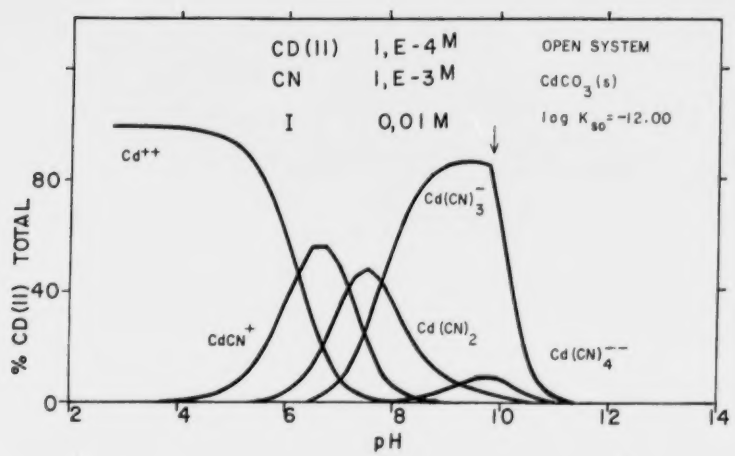
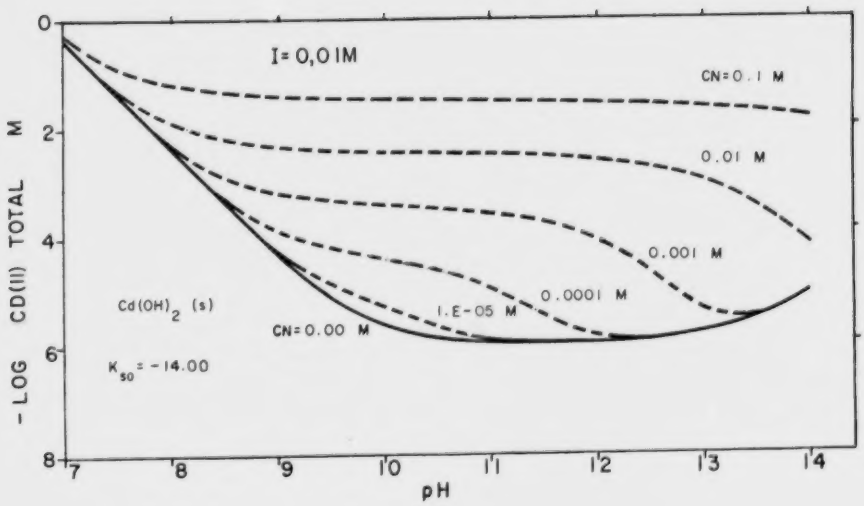


Figure 2. Aqueous chemistry of Cd-CN solution.

a. Solubility of $CdCO_3$(s) in the presence of CN.
b. Speciation of Cd(II) species in the presence of $CdCO_3$(s).



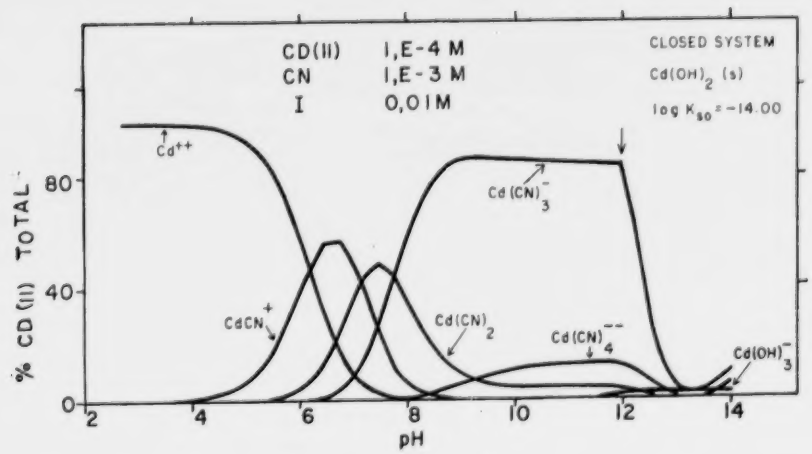


Figure 3. Aqueous chemistry of Cd-CN solution.

a. Solubility of $Cd(OH)_2(s)$ in the presence of CN.
b. Speciation of Cd(II) species in the presence of $Cd(OH)_2(s)$.

In most of the experimental work, the test solutions involving the cadmium cyanide wastewater contained a total cadmium concentration of 10^{-4} moles/ℓ and a total cyanide concentration of 10^{-3} moles/ℓ. These values were used in computing the speciation diagram. It should be noted that the fraction of total cyanide available for complexation, or free cyanide, is itself a function of pH related by an acidity constant, K_a. The stability constants used in the solubility and speciation distribution computations are listed in Table 3.

TABLE 3. Common Equilibrium Reactions of Cd(II) and Its Related Species in Aqueous Solution (35)

Reaction	Log K
$(CdOH^+) = K_1 (Cd^{+2})(OH^-)$	9.16
$[Cd(OH)_2] = \beta_2 (Cd^{+2})(OH^-)^2$	8.39
$[Cd(OH)_3^-] = \beta_3 (Cd^{+2})(OH^-)^3$	9.08
$[Cd(OH)_4^{-2}] = \beta_4 (Cd^{+2})(OH^-)^4$	8.76
$(CdCN^+) = K_1 (Cd^{+2})(CN^-)$	6.02
$[Cd(CN)_2] = \beta_2 (Cd^{+2})(CN^-)^2$	11.15
$[Cd(CD)_3^-] = \beta_3 (Cd^{+2})(CN^-)^3$	15.71
$[Cd(CN)_4^{-2}] = \beta_4 (Cd^{+2})(CN^-)^4$	13.03
$(CdCN) = K (Cd^+)(CN^-)$	9.21
$(CdNH_3^{+2}) = K_1 (Cd^{+2})(NH_3)$	3.65
$(Cd(NH_3)_2^{+2}) = \beta_2 (Cd^{+2})(NH_3)^2$	9.75
$(Cd(NH_2)_3^{+2}) = \beta_3 (Cd^{+2})(NH_3)^3$	6.19
$(Cd(NH_3)_4^{+2}) = \beta_4 (Cd^{+2})(NH_3)^4$	7.12
$(Cd(NH_3)_5^{+2}) = \beta_5 (Cd^{+2})(NH_3)^5$	6.80
$(Cd(NH_3)_6^{+2}) = \beta_6 (Cd^{+2})(NH_3)^6$	5.14
$(NH_4^+) = K (H^-)(NH_3)$	9.25
$K_{so} = (Cd^{+2})(OH^-)^2$	-14.00
$K_{so} = (Cd^{+2})(CO_3^{-2})$	-12.00
$(H_2CO_3^*) = K_H P_{co2}$	-1.5
$(HCO_3^-) = K_1 (H^+)(CO_3^{-2})$	10.25
$(H_2CO_3^*) = \beta_2 (H^+)^2(CO_3^{-2})$	16.55
$K_{so} = (H^+)(OH^-)$	-14.00

For Cd(II) = 10^{-4}M and CN = 10^{-3} M, the solubility diagrams indicate that $CdCO_3$(s) will not precipitate until about pH 10 (Fig. 2a) while $Cd(OH)_2$ precipitation should not be a factor at all (pH 12, Fig. 3b). However, experimental results using the stated initial conditions show that some cadmium is removed by precipitation, the onset occurring already at approximately pH 7.5 (Fig.4). This apparent inconsistency can be explained as a problem involving the kinetics of precipitation. In obtaining the precipitation data, the samples were reacted for 48 hours to insure equilibrium. Tests on identical solutions using the ion specific electrode revealed that the free cadmium (Cd^{+2}) concentration increased slowly over time, in the pH range of 8 to 10, to almost 10^{-4} M which is the total Cd(II) concentration. This indicates that the cyanide is coming out of solution over time, perhaps reducing to

as low as a 1:1 cadmium to cyanide ratio, or 10^{-4} M. At this cyanide concentration, we would expect $CdCO_3(s)$ precipitation at about pH 7 to 7.5, and $Cd(OH)_2(s)$ begins to precipitate at pH 10.5. The experimental data seems to bear this out, with initial precipitation at pH 7 and a substantial increase in removal at pH 11.

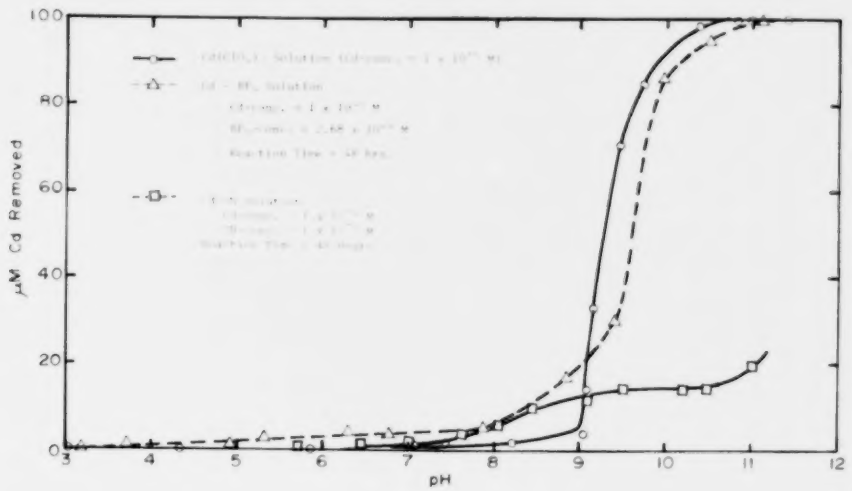


Figure 4. Precipitation of Cd(II) from $Cd(ClO_4)_2$ solution (o), Cd-BF_4 solution (Δ) and CdCN solution (□).

The aqueous chemistry of the cadmium fluoborate system is more difficult to analyze. The equilibria involved in the formation and hydrolysis of the tetrafluoroborate ion (BF_4^-) are extremely complex and only recently have been adequately investigated. The anionic species present in a fluoroborate bath are $BF_3(OH)^-$, $BF(OH)_3^-$ and $B(OH)_3$ (36).

The tetrafluoborate ion is similar in volume, structure, and chemical behavior to the perchlorate ion (37), which tends to remain uncoordinated with metal ions in aqueous solutions (38). Tetrafluoborates contain the ion in which boron is covalently saturated by fluorine and, since fluorine does not generally form a covalent link between two atoms, this ion can be relied upon to form salts in which there is a true cation, e.g., Cd^{+2}, with no covalent bonding to the anion (36). Thus cadmium does not form stable complexes with the BF_4^- ion as it does with CN^-, but the two (i.e., Cd^{+2} and BF_4^-) can exist in an ion pair relationship. In this case, the metal ion or the ligand or both retain the coordinated water in forming the "complex," that is, the Cd^{+2} cation and the BF_4^- anion are separated by one or more water molecules (39). Figure 5a shows that nearly 50 percent of the "free" Cd^{+2} is bound to BF_4^- anions, probably as $Cd(H_2O)_6(BF_4)_2$, which is one of only a few cadmium fluoborates reported in the literature. It is noted that the aqueous Cd(II) chemistry in Cd-BF_4 solution is close to a $Cd(ClO_4)_2$ or a Cd-NH_4 solution.

The data also show that ammonium, although a relatively strong metal complexing agent, is not present in the plating solution at sufficiently high concentrations to compete with the BF_4^- anion, whose concentration in solution is more than four times as great. Thus it does not form complexes with cadmium in this solution. Based on this observation, the speciation of cadmium species in cadmium tetrafluoborate solution is calculated and shown in Figure 5b.

Cadmium precipitation data for the cadmium fluoborate plating wastewater compared with that in a $Cd(ClO_4)_2$ solution is shown in Figure 4. Cadmium removal by precipitation is much greater here than in the cyanide system, where Cd^{+2} was strongly complexed to the CN^- ligand. Precipitation from the fluoroborate solution is similar to that for perchlorate, except that the "jump" in removal for the former occurs at a slightly higher pH value, and approaches 100 percent (in terms of cadmium removal) at pH 11. This is an important observation for considering chemical precipitation and adsorption as possible cadmium removal processes.

Appendix 1 shows formulations relevant to equilibrium calculations of aqueous Cd(II) chemistry.

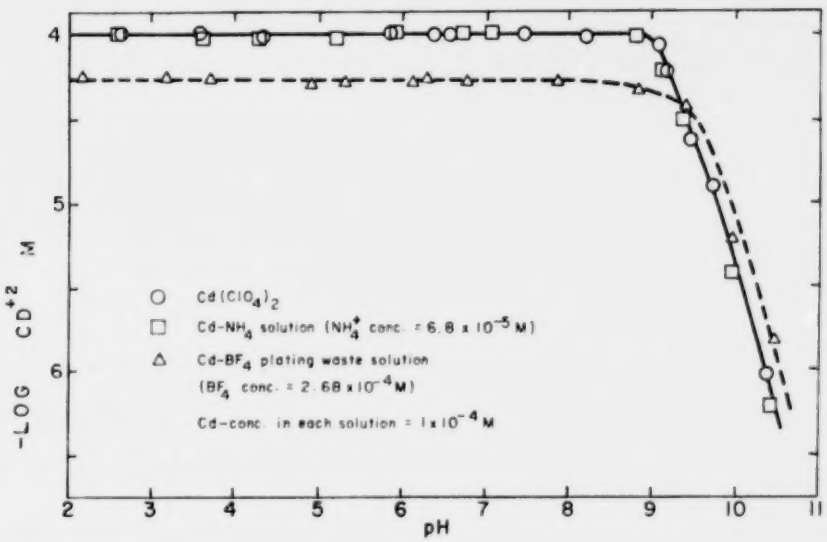


Figure 5a. The concentration distribution of free Cd^{2+} species in various solutions.

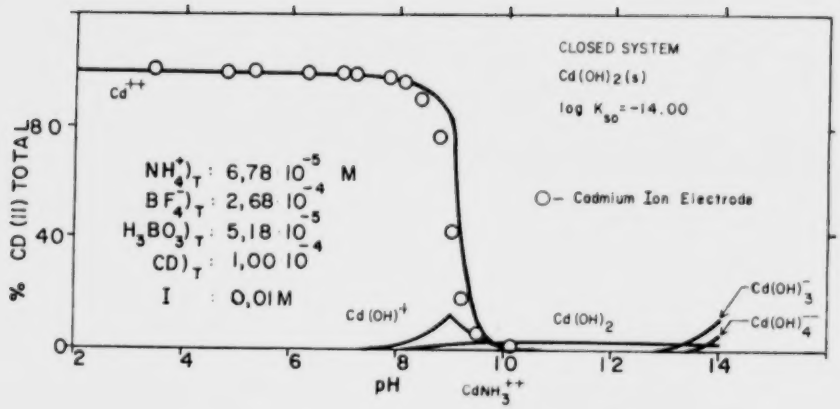


Figure 5b. The chemical speciation of a Cd-BF_4 solution.

SECTION 5

BATCH MODE STUDIES

Regardless of the system in which adsorption is to be used, there are two distinct aspects of adsorption which must be considered in the design of processes to be used for wastewater treatment. One of these aspects is the kinetics or rate of adsorption; the second is the extent or ultimate capacity for adsorption, referred to as adsorption equilibria (40). The factors examined in this study that may affect one or both of these aspects were ratio carbon dose/Cd(II) concentration, the presence of other chemicals in solution, pH, ionic strength of solution, temperature, and carbon type.

As indicated in Section 4, a representative Cd(II) concentration for electroplating wastewaters is 1×10^{-4} moles/ℓ or 11.24 ppm. This is the value used in kinetics studies. In order to obtain adsorption isotherms for the modeling of the extent of adsorption, the original Cd(II) concentration was varied from 5×10^{-5} to 5×10^{-3} moles/ℓ (or 5.62 to 562.0 ppm). Since nearly all cadmium plating is done in either the cyanide or fluoborate baths, these were the two model systems studied. A molar ratio of 1:10, cadmium to cyanide, was used for the cyanide system, this value being consistent with those reported in the literature for cadmium plating wastewaters. The cadmium fluoborate wastewater contains ammonia and boric acid, in addition to the various species believed to be present as a result of hydrolysis of the tetrafluoborate ion.

The pH range studied in this work is approximately 3 to 10. The pH of the fluoborate wastewater is about 4, while that of the cyanide system is around pH 10, depending on the initial cadmium concentration. An ionic strength of 0.1 M as $NaClO_4$ was used in all of the experimental work. This value is probably high for cadmium industrial wastewaters, but, as will be shown, gives adsorption results that are "conservative", a desirable condition for system design purposes. Both kinetics and equilibrium experiments were conducted at various temperatures, ranging from 10 to 50 °C. This is well in excess of the temperature range encountered in actual wastewater treatment.

In addition to adsorption experiments, desorption experiments were also conducted to gain information on the regenerability of Cd(II)-laden activated carbon. Finally, an attempt was made to enhance the adsorptive capability of some specific activated carbon by pretreatment with liquid carbon disulfide.

EXPERIMENTAL

Activated Carbons

The carbons used for this study were obtained from three sources. The Filtrasorb series along with Pittsburgh HGR were obtained from Calgon Corporation. The Darco series were obtained from ICI-USA Chemical Industries, Inc., and the Nuchar brands were obtained from the Westvaco Corporation. Unless otherwise specified, all activated carbons were used as received. Various surface characteristics of these carbons are presented in Table 4.

Chemicals

Cadmium fluoborate and cadmium cyanide plating wastewaters were prepared as 10^{-2} M cadmium stock solutions using reagent grade chemicals. These synthetic plating waste solutions were made so as to simulate actual cadmium plating systems. Table 1 gives the make-up of typical cadmium plating baths. These values were then proportionally scaled down to prepare the more dilute stock solutions (Table 5).

Reagent grade chemicals were also used to prepare 1.0 M $HClO_4$ and 1.0 M NaOH for pH adjustment, and 1.0 M $NaClO_4$ for providing ionic medium. Deionized-distilled water was used in the preparation of all solutions.

TABLE 5. Composition of Stock Solutions*+

Cadmium Perchlorate	
CdO	1.284 gm
$HClO_4$ (1 M)	10 mℓ
Cadmium Cyanide Bath†	
CdO	1.284 gm
NaCN	5.4 gm
Cadmium Fluoborate Bath§	
CdO	1.284 gm
$HClO_4$ (1 M)	10 mℓ
HBF_4 (40%)	3.608 gm
$NH_4(BF_4)$	0.711 gm
$H_3(BO_3)$	0.320 gm

*All stock solutions have a Cd(II) concentration of 10^{-2} M.
†Molar Ratio Cd:CN = 1:10.
§Molar Ratio $Cd:BF_4:NH_4:H_3BO_3$ = 1:2.7:0.7:0.5
+Added to one liter.

Adsorption Experiments

Batch kinetics experiments were conducted by adding given amounts of activated carbon to 500 mℓ of synthetic cadmium wastewater solution in 1000 mℓ

TABLE 4. Typical Physical-Chemical Properties of Activated Carbon (41)

Manufacturer	Carbon Type	Iodine Number (mg/g)	Surface Area N_2 BET	Surface Area (m^2/g)	Total Pore Volume (cm^3/g)	Average Diameter (mm)	Ash %	Water Soluble %	pH_{zpc}
CALGON	Filtrasorb								
P.O. Box 1346	100	> 850	850- 950	950	--	--	4.3	--	6.5
Pittsburgh, PA	200	> 850	850- 900	925	--	--	3.6	--	--
15230	300	> 900	950-1050	900	--	1.5-1.7	11.1	0.5	--
	400	>1000	950-1050	1100	--	0.9-1.1	5.1	0.5	7.0
ICI	Darco G-60	--	--	--	--	--	1.4	0.3	--
Wilmington, DE	KB	--	1500	--	1.5	--	2.6	1.5	--
19897	S-51	--	650	600	1.0	--	19.2	1.5	--
	T-70	900	1000-1100	--	0.9	--	<6.0	--	--
	Hydro Darco								
	3000	550	550- 650	550	1.0	1.4-1.6	21.0	--	5.5
	C	--	550	--	--	--	28.2	5.5	--
WESTVACO									
Covington, VA	Nuchar SA	> 800	1400-1800	700	--	--	5.3	3-4	3.7
24426	SN	> 800	1400-1800	1400	--	--	5.0	3-4	4.2
	WVG	>1050	>1100	900	--	0.90-1.20	6.1	--	--
	WVL	> 950	>1000	1250	--	1.4-1.7	7.0	--	7.5
	WVW	> 850	> 910	925	--	--	4.8	--	--

pyrex beakers. The Cd(II) concentration was 10^{-4} M (11.2 ppm), in order to simulate a typical cadmium plating wastewater, and the ionic strength was 10^{-4} M as $NaClO_4$. Continuous mixing was achieved by using a magnetic stirrer. The pH was adjusted with 1.0 M $HClO_4$ or NaOH solution and recorded with a digital pH meter (Beckman, pHasar-I) equipped with a combination electrode (Markson, pHexi Mark, 2888). At predetermined time intervals, 10 mℓ of sample were pipetted from the reactor and filtered through an 0.45 micron filter membrane to separate the carbon from solution.

Batch equilibrium data were obtained by placing measured amounts of carbon into 100 mℓ samples of cadmium solution using 125 mℓ polypropylene bottles as reactors. For a given initial Cd(II) concentration (ranging from 5×10^{-5} M to 5×10^{-3} M), the pH of the samples was adjusted to cover a pH range of approximately 3 to 10. The samples were then agitated in a reciprocating shaker for 24 hours (unless indicated otherwise) at room temperature (26 °C). After shaking, the pH was recorded and an appropriate volume of sample was obtained by filtering through an 0.45 micron membrane.

Both kinetic and equilibrium data were obtained for various temperatures. Temperature control was provided by using the B. Braun Thermomix 1460-Frigomix 1495 and the American Optical Water Bath Shaker units.

Desorption Experiments

Desorption experiments were conducted in batch reactors. After the last adsorption sample was taken from a reactor, the carbon was separated from solution by filtration and then washed into a clean reactor with a solution similar to the previous one (in terms of pH, ionic strength, and temperature), except without any Cd(II). At the end of desorption time, which was taken to be as long as the adsorption time, the amount of previously adsorbed Cd(II) was determined employing the same analytical procedure used in adsorption studies.

Pretreatment of Activated Carbon

One of the granular carbons, Darco HD 3000, was pretreated with carbon disulfide (CS_2) with the intent of enhancing cadmium adsorption. First, 3.0 gm of sodium methylate (CH_3ONa) were placed in a round bottom flask and then dissolved in methanol. After refluxing this solution for 10 minutes, 15 gm of activated carbon were added and the new mixture refluxed for 6 hours. The methanol was then evaporated slowly, followed by the addition of 15 mℓ of liquid CS_2 and hexane, and 6 hours more of refluxing. The treated carbon was separated by filtration and then washed, first with small amounts of hexane followed by washing thoroughly with deionized-distilled water. After drying, the carbon was used in kinetics and equilibrium experiments, and the results were compared with those for the untreated carbon.

Cadmium Analysis

The residual Cd(II) concentrations were determined by flame atomic adsorption spectroscopy, using the Jarell Ash Model 810 spectrophotometer (air/acetylene flame, and primary wavelength = 2288 Å). This gives a measure of the total residual Cd(II) concentration, including both free Cd^{+2} and any

soluble metal complexes, e.g., $Cd(CN)_2$, $Cd(BF_4)_2$. Cadmium calibration standards were prepared with the same chemical composition as test samples in order to prevent matrix interference effects.

Free Cd(II) Determination

Experiments were done to determine free Cd^{+2} as a function of pH for both the cadmium fluoborate and cadmium cyanide systems. Several 100 mℓ samples containing 1×10^{-4} M Cd and 0.1 M ionic medium were placed in 125 mℓ polypropylene bottles. The pH was adjusted to cover a pH range of approximately 3 to 11. The samples were then agitated for 48 hours in a reciprocating shaker at room temperature. After shaking, the pH value was recorded, followed by free Cd^{+2} analysis using the model 801A Digital Ionalyzer from Orion Research equipped with a cadmium specific ion electrode (Orion Research Model 94-48 A). Calibration standards were made from a 10^{-2} M cadmium perchlorate stock solution prepared from the metal perchlorate salt, $Cd(ClO_4)_2 \cdot 6H_2O$. Following the free Cd^{+2} analysis, an appropriate volume of sample was taken from each reactor and analyzed for total cadmium using atomic adsorption in order to determine the amount of cadmium removed from solution by precipitation.

Electrophoretic Mobility

Electrophoretic mobility of activated carbons was determined using the zeta-meter manufactured by Zeta-Meter, Inc. Solutions of carbon were made at various pH values ranging from 2-10. The solutions were then placed in the Riddick cell, individually, and the electrophoretic mobility determined for the corresponding pH value. The pH_{zpc} was determined where mobility of the particles was zero.

RESULTS AND DISCUSSIONS

Surface Characteristics

The adsorption of cadmium onto activated carbon has been studied by previous investigators (19,20). The mechanisms believed to be responsible for the carbon's affinity for cadmium are both chemical and physical. Physical parameters such as specific surface area and pore size and distribution determine what capacity an adsorbent can have for an absorbate and whether or not the adsorbate is capable of diffusing into the pores and being adsorbed on the surface at the active surface sites. If the physical size of the adsorbate is larger than a majority of the pore channels, a large portion of the surface sites are cut off from the adsorbate. Chemical parameters are important in determining an adsorbent's surface affinity for a particular adsorbate. In the case of activated carbon, cadmium adsorption behavior is not identical for various types of carbon, even with relatively identical surface area. This indicates other factors come into play regarding cadmium adsorption. Huang and Ostovic (19) attributed variations in adsorption behavior to the differences in surface acidity.

Most carbons are similar in structure to turbostratic carbon, denoting an irregular microcrystalline structure in contrast to a very ordered graphite

lattice. The level of structural imperfections in activated carbon microcrystallites (usually a few layers thick and less than 100 Å in width) is very high, which results in many possibilities for reactions of the edge carbons with their surroundings (24). The edge reactions of activated carbon are not specifically known but nearly every type of functional group known in organic chemistry has been suggested as being present on the surface of activated carbon (24). Assuming that a large portion of these functional groups are affected by solution characteristics, such as pH and ionic medium, a dependent electrostatic charge of the surface should be observed. Electrophoretic mobility is a method of characterizing the charge of a surface as a function of pH. Figure 6 illustrates the electrophoretic mobility of activated carbons as a function of pH. It was found in this study that carbon adsorption of cadmium, under identical conditions, was greatest for the carbon with the lowest pH_{zpc} and less adsorption occurred for carbons with higher pH_{zpc}'s. This suggests that Nuchar SA and Nuchar SN have a predominant

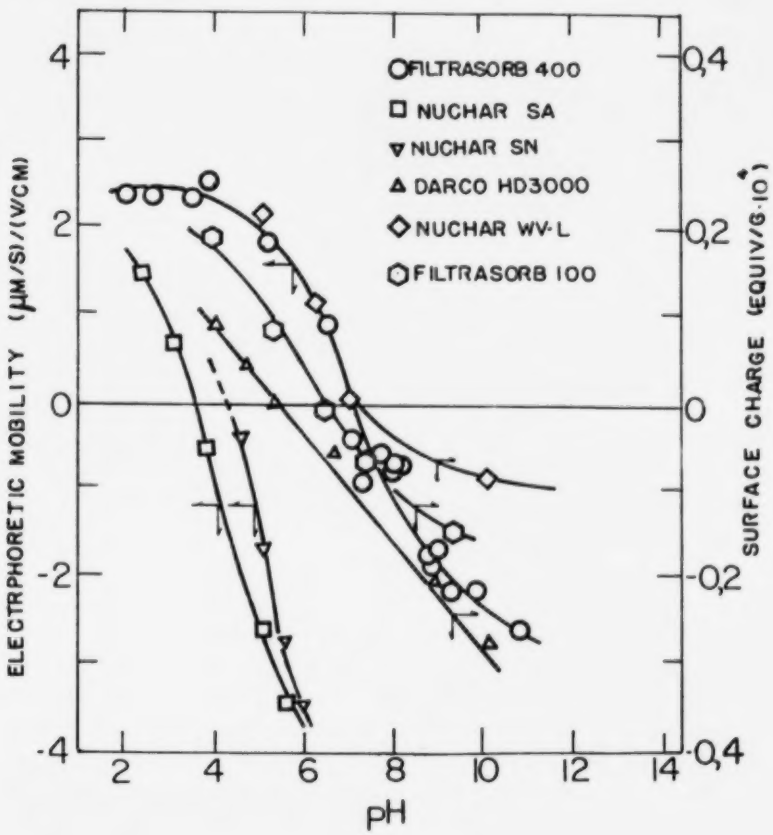


Figure 6. The electrophoretic mobility of various activated carbon as a function of pH; the point of pH at which the electrophoretic mobility is zero is pH_{zpc} (41).

negatively charged surface since the major cadmium species present for pH 7.0 is Cd^{+2} (aq). Therefore a large portion of the surface functional groups must be negatively charged in the pH range > pH_{zpc}. This partially explains the adsorptive characteristic of the various activated carbons.

Preliminary Screening Studies

Preliminary screening studies were performed for a total of fifteen different types of activated carbons concerning their Cd(II) removal capacity. Table 6 gives the results of the preliminary Nuchar SA and Nuchar SN, exhibiting a far greater removal efficiency than the granular carbons. This finding is in agreement with what was reported by Huang and Ostovic (19). Results from Huang et al. (42) illustrated in Figure 7 show the dependence of adsorption on pH. A similar behavior is shown for both the two powdered and granular carbons; adsorption of cadmium increasing with increasing pH and degree of removal related to the pH_{zpc} of the appropriate carbon. All of the studies in Table 6 and Figure 7 were performed with a synthetic $Cd(BF_4)_2$ waste water.

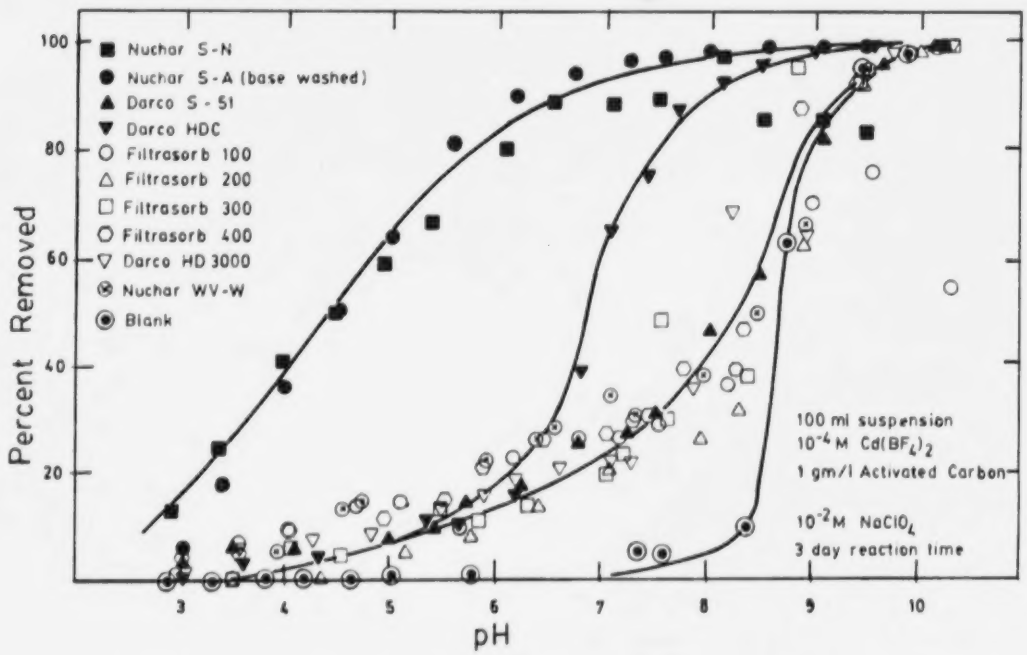


Figure 7. Effect of carbon type on Cd(II) removal.

As for the selection of activated carbons, initial tests showed two powdered carbons, Nuchar SN and Nuchar SA, to be very effective in removing Cd(II) from solution. As a result, these were both chosen for more detailed investigation. Fourteen different brands of granular activated carbon were also tested, and none were found to compare favorably with either of the powdered carbons selected (Table 6). From these eight, two representatives

TABLE 6. Percent Cd(II) Removal of Various Types Activated Carbon*

Carbon	pH	Carbon Dose (g/ℓ)	Reaction Time (hr)	Ionic Strength (M $NaClO_4$)	% Removal
Calgon Co.					
Filtrasorb					
100	7	1	24	10^{-2}	21
	7	1	72	10^{-2}	25
200	7	1	24	10^{-2}	21
	7	1	72	10^{-2}	22
300	7	1	24	10^{-2}	21
	7	1	72	10^{-2}	22
400	7	1	24	10^{-2}	17
	7	1	72	10^{-2}	25
	8.9	2.8	24	10^{-1}	46
Pittsburgh HGR	7	1	24	10^{-2}	6
ICI, Inc.					
Darco HDC 3000	7	1	72	10^{-2}	21
	7	1	24	10^{-2}	25
12 x 20	7	1	24	10^{-2}	26
	7	2.8	2	10^{-1}	37
12 x 40	7	1	24	10^{-2}	26
	7	2.8	2	10^{-1}	44
20 x 40	7	1	24	10^{-2}	26
	7	2.8	2	10^{-1}	44
5-51	7	1	72	10^{-2}	30
HDC	7	1	72	10^{-2}	21
Westavaco					
Nuchar SN	7	1	24	10^{-2}	67
	7	1	72	10^{-2}	90
Nuchar SA	7	1	24	10^{-2}	83
	7	1	72	10^{-2}	92
WV-W	7	1	24	10^{-2}	10
	7	1	72	10^{-2}	30
WV-G	7	1	24	10^{-2}	23
WV-L	7	1	24	10^{-2}	22

*From synthetic Cd-BF_4 solution.

were chosen for purposes of comparison. One of these, Filtrasorb 400, has been demonstrated to be an effective adsorbent for the removal of hexavalent chromium from industrial wastewater (43,44). The other, Darco HD 3000, is a recently marketed carbon and has the largest particle size of those examined. In addition, an attempt was made to alter the surface of one of the granular activated carbons in order to enhance its adsorption capability.

Kinetics of Cadmium Adsorption

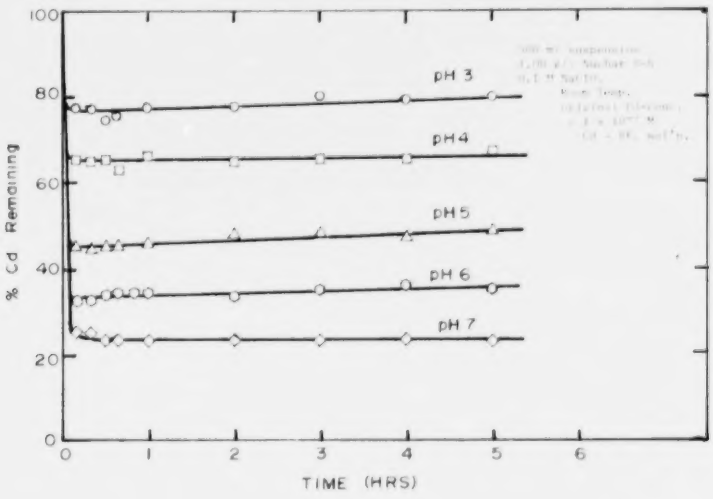
The rate of adsorption of any solute from solution onto activated carbon is governed by three consecutive steps (45,46). Whichever of these offers the most resistance to adsorption is considered to be the rate-limiting step. For this study, the first step would involve the diffusion of the Cd(II) species through a liquid boundary layer or film surrounding the surface of the carbon particle in solution. If the resistance to mass transfer of Cd(II) ions at the carbon is high, then this "film diffusion" will be the rate-determining step in the adsorption process. However, when adequate mixing is provided to the system, film diffusion is generally not a problem.

The second step in adsorption would be the penetration and diffusion of Cd(II) through the pores of the activated carbon. Obviously the pore size distribution of the carbon and the size and structure of the Cd(II) species being adsorbed are important factors to consider here.

The final step is the reaction of the Cd(II) ion or molecule with the carbon surface, i.e., adsorption. Several theories have been developed to describe and model this adsorption of metal ions at solid-solution interfaces (19). Among them are the Gouy-Chapman-Stern-Grahame model, which describes adsorption as resulting from specific and electrostatic interactions, and the surface complex formation model, in which the surface groups (i.e., C-OH) are treated as complex forming agents. This aspect will be dealt with in more detail in the discussion of the extent of adsorption. When speaking of the kinetics of adsorption, however, the adsorption reaction is rarely the rate-limiting step.

In fact, upon examining the experimental data, it appears that cadmium adsorption with activated carbon is not at all kinetically limited. Figure 8a depicts the rate of adsorption of cadmium from a fluoborate plating waste solution using Nuchar SN, a powdered carbon, as the adsorbent. It is evident that the reaction proceeds very fast at all pH values considered. The initial samples were taken at ten minutes after contact of the carbon with solution. From Figure 11a it appears that equilibrium has effectively been reached by this point in time. Therefore, additional experiments were conducted in which samples were taken every two minutes for the first ten minutes of reaction. These results are shown in Figure 8b which is a plot of percentage of Cd remaining in solution versus the time in minutes for a cadmium fluoborate wastewater using Nuchar SA as the adsorbent. This data points out that the maximum adsorption level is reached within the first two minutes of reaction, or the time just beyond that required for pH adjustment.

Obviously, then, pore diffusion and the adsorption step are not rate-controlling. The only remaining possibility is that the mixing rate in the reaction vessels is a critical parameter, implying that film diffusion is the rate-determining step. The mixing rate employed in all of the kinetics work was 550 rpm using a magnetic stirrer with a 1-1/4" x 3/8" mixing bar in 500 mℓ of suspension. One series of experiments varied the mixing rate to determine its effect, and the results are presented in Table 7. The data clearly indicate that the adsorption rate is not appreciably changed by a change in mixing rate, and therefore is not limited by film diffusion.



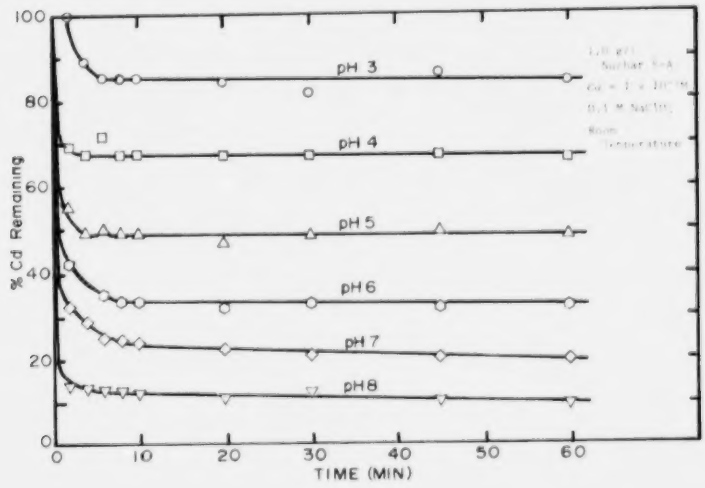


Figure 8. Kinetics of Cd(II) adsorption from Cd-BF_4 solution onto activated carbon. Effect of pH. (a) Nuchar SN (top); (b) Nuchar SA (bottom).

Consequently, it is nearly impossible to obtain a meaningful mathematical expression for the rate of cadmium adsorption in the system being studied, since the removal is occurring essentially at contact. Nor would it serve any practical purpose, since the reaction is clearly not rate limited.

Figures 7 and 8 also point out that a change in pH has no significant impact on the rate of adsorption. Regardless of the pH value, the reaction is still extremely rapid. (The only exception may be the case of pH=3 in Figure 8b. This plot indicates almost no removal after 2 minutes of reaction.

TABLE 7. Cadmium Removal (%) from Solution for Various Mixing Rates

Time	350 rpm	450 rpm	550 rpm	650 rpm
10 min	38.0	38.5	37.5	35.0
20 min	37.0	37.5	40.0	34.5
30 min	39.0	37.5	40.0	35.5
45 min	36.5	36.5	38.5	37.5
1 hr	36.1	36.5	37.5	33.5
2 hr	35.0	34.5	35.0	35.5
3 hr	35.0	36.1	34.0	34.5
4 hr	--	33.5	33.0	34.5
5 hr	--	37.0	33.0	33.0

Experimental Conditions: Cd-BF_4 Solution; 1.0 g/ℓ Nuchar SN; 0.1 M $NaClO_4$; pH = 4; Original Cd-concentration = 1×10^{-4} M; Room temperature; 500 mℓ suspension; 1000 mℓ reactor; 1½" x 3/8" mixing bar.

However, the removal at this pH value is small anyway, and the pH may not have been properly adjusted at this time causing an error in the resulting data point. Also, the removal has reached its maximum value after just 6 minutes, indicating a rapid removal rate under the stated conditions.) The pH of the cadmium fluoborate plating wastewater, initial Cd(II) concentration 1×10^{-4} M, before adding the activated carbon was 3.80. The pH after the addition of the carbon varied according to the carbon type and dosage. For a 1.0 g/ℓ dose of Nuchar SN, the pH of the solution rose to approximately 5.90, while an identical dose of Nuchar SA altered the pH only slightly, to about 3.95. This reveals that the surface of the Nuchar SA particles is more acidic than that of Nuchar SN, a fact which is consistent with the pH_{zpc} values of 3.80 for Nuchar SA and 5.84 for Nuchar SN (where the pH of zero net charge is designated as the pH_{zpc}). At this point, the pH was adjusted and maintained at the desired value by periodic additions of acid or base. For the powdered carbons, these adjustments were not difficult, as the pH drift over time was minimal.

It is also clear from the data in Figure 8 that pH is an important factor with regard to the extent of cadmium removal by adsorption, with increasing removal for increasing pH in fluoborate wastewater. For the case where Nuchar SA is used as the adsorbent (8b), the amount adsorbed at pH 8 is nearly six times as great as that removed at pH 3.

Figure 9 compares the rate of uptake of cadmium from the fluoborate system for four activated carbons. This demonstrates the superiority of the powdered carbons over the granular ones in terms of the extent of Cd(II) removal. Also, the rate of uptake is somewhat slower for the granular carbons. This is consistent with results reported by others using granular activated carbons as adsorbents, characterized by a relatively rapid initial

rate of adsorption followed by a slower, more gradual approach to equilibrium. There is much experimental evidence to support the theory that pore diffusion is the rate-limiting step for granular activated carbon adsorption (47), particularly in batch reactors where turbulence due to mixing is generally sufficient to eliminate any difficulty in film transport. According to information provided by the manufacturer, the powdered carbons contain a large preponderance of pores in the transitional and macropore range, as opposed to the micropore structure of most granular carbons. This system of macropores would tend to make interparticle transport of the adsorbing species much easier, and bring about more rapid utilization of the ultimate capacity of the carbon.

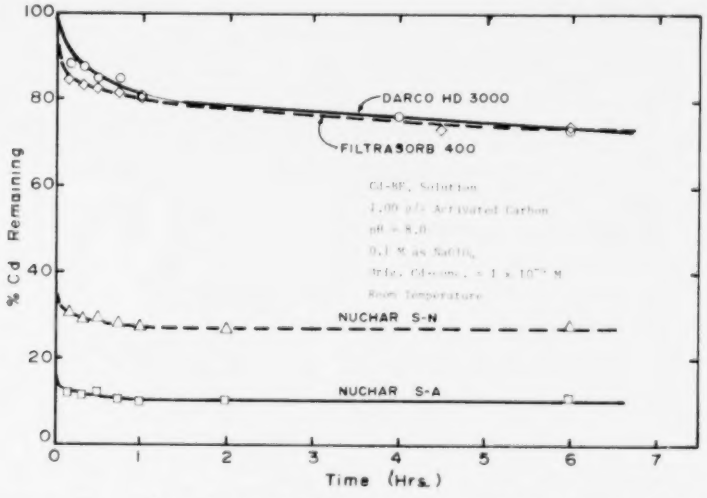


Figure 9. Kinetics of Cd(II) adsorption from Cd-BF_4 solution as affected by carbon type.

The kinetics of cadmium adsorption from the cyanide wastewater using powdered carbons is similar to that in the fluoborate system, and is depicted in Figure 10. Once again, the reaction is extremely rapid, with adsorption approaching the maximum level within the first 10 minutes of contact. However, two major differences between the two systems are apparent. One is that the extent of removal for comparative pH values is not as great from the cadmium cyanide solution. The other is that, while cadmium adsorption increases with pH up to pH 6.5, the removal is substantially less at pH 8.5 in the cyanide solution. This indicates that there is an adsorption "peak" in the adsorption versus pH relationship for the cadmium cyanide system, in contrast with the fluoborate solution which shows steadily increasing removal with increasing pH. Both of these issues will be presented and discussed in greater detail in the section dealing with adsorption equilibria.

Weber and Morris (45) reported that the rate of adsorption from solution is essentially independent of carbon concentration. The data shown in Figure 11 for adsorption from the cadmium fluoborate solution exhibits this characteristic. For the same initial Cd(II) concentration, the kinetics are virtually unchanged regardless of the carbon/cadmium ratio. In this case,

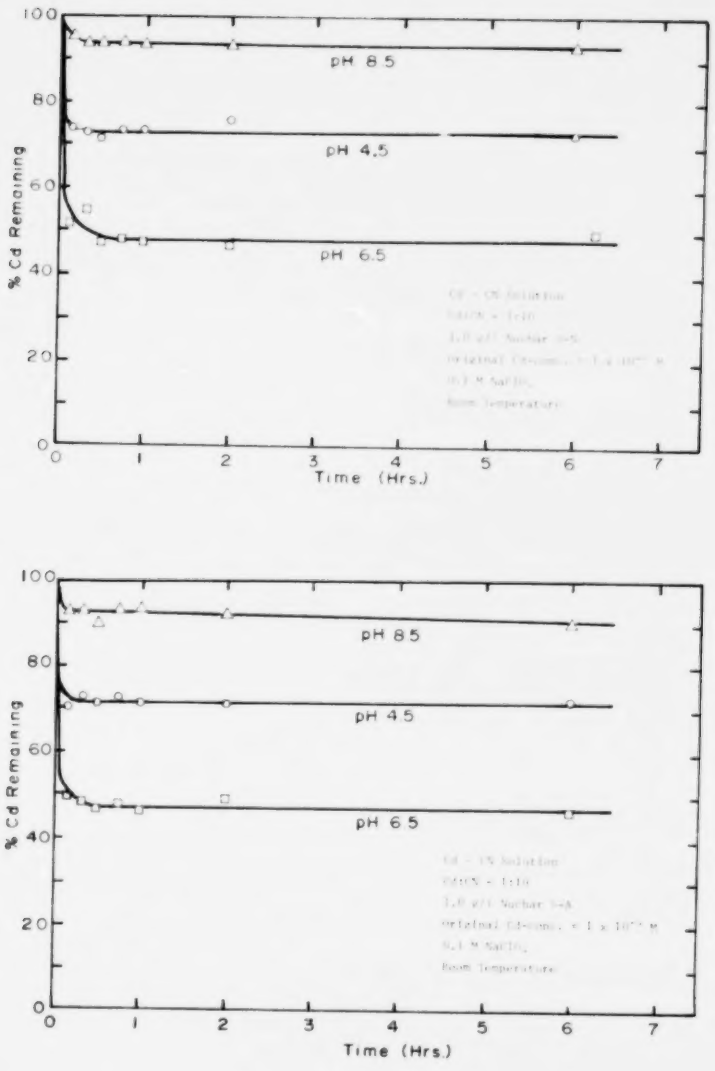


Figure 10. Kinetics of Cd(II) adsorption from Cd-CN solution onto activated carbon. Effect of pH. (a) Nuchar SN (top); (b) Nuchar SA (bottom).

a carbon/cadmium ratio of 89 (by weight) is equivalent to a carbon dosage of 1.0 g/ℓ, a ratio of 178 is equivalent to 2.0 g/ℓ, and so on.

Another parameter of importance in adsorption is the ionic strength of the wastewater. Figure 12 is a plot of percent Cd(II) remaining and time for different ionic strength values in a cadmium cyanide wastewater. Although decreasing the ionic strength certainly increases the equilibrium adsorption of cadmium from solution, there is no apparent change in the rate of removal for varying molar concentrations of ionic medium.

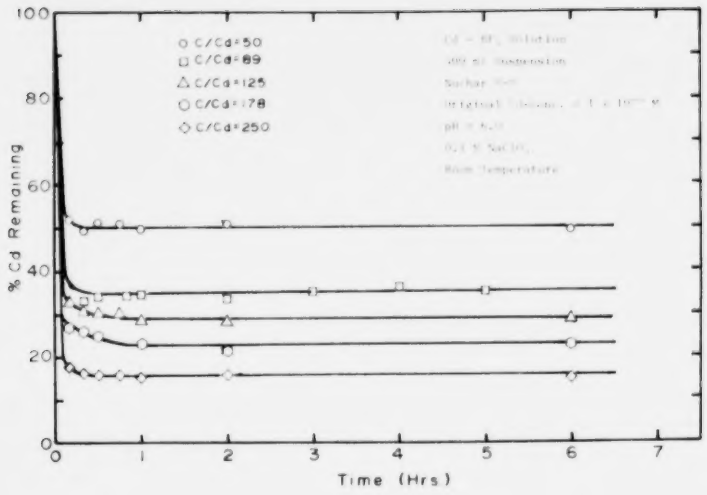


Figure 11. Kinetics of Cd(II) adsorption from Cd-BF_4 solution onto activated carbon as affected by carbon-to-Cd(II) ratio; C/Cd ratio expressed in mg/mg.

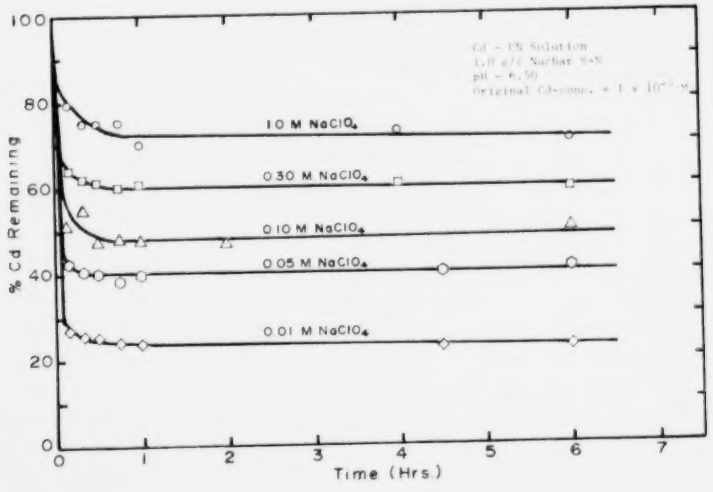


Figure 12. Effect of ionic strength on the kinetics of Cd(II) adsorption from Cd-CN solution onto activated carbon.

Finally, the nature of the rate-determining step in a chemical reaction involving adsorbents can also be characterized by its activation energy (45). The activation energy can be determined by examining the relationship between

adsorption rate and temperature. However, the data in Figure 13 shows no apparent change in the adsorption rate for a change in temperature. This was true for all of the systems studied in this work.

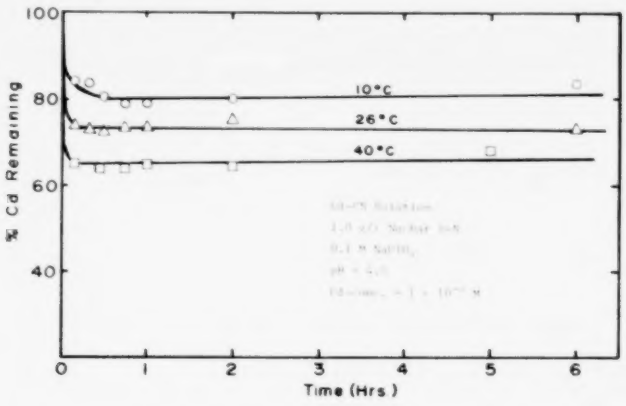


Figure 13. Effect of temperature on the kinetics of Cd(II) adsorption from Cd-CN solution onto activated carbon.

In summary, the kinetics of cadmium adsorption from both the cyanide and fluoborate plating wastewaters are quite simple, from a practical standpoint. The reaction proceeds very fast, almost always reaching the maximum level within the first few minutes of contact of carbon with the wastewater. Varying such parameters as pH, carbon dose, the ionic strength of solution, and temperature do not change the rate of removal. The only kinetically significant variable appears to be the type of carbon used, with the powdered carbons attaining equilibrium removal more rapidly than granular brands. The extremely rapid initial removal rate is an attractive feature of the activated carbon adsorption process for the treatment of cadmium plating wastewaters and encourages further investigation as the extent of removal.

Significance of Carbon Type

For a particular carbon to be effective as an adsorbent, it must not only provide a rapid rate of cadmium removal from solution, but its ultimate adsorption capacity must also be large. Kinetic data has already suggested that powdered activated carbons, in particular Nuchar SN and Nuchar SA, have a rather large cadmium adsorption capacity as compared to granular brands such as Filtrasorb 400 and Darco HD 3000. Figure 14 illustrates this tendency even more conclusively. The ordinate, Γ, is a measure of the adsorption density, expressed as micromoles of Cd(II) adsorbed per gram of carbon, or $\mu M/g$. The results show that Nuchar SA affords up to 90-95 percent Cd(II) removal in the neutral pH range. This is approximately 3 times as great as that achieved with the granular carbons. As indicated, the data in Figure 14 were obtained after 2 hours reaction time. Results from kinetics experiments showed that samples taken after 2 hours give a good approximation of the equilibrium

adsorption value when powdered carbons are used as adsorbents. As for the granular carbons, the actual equilibrium values are slightly higher than those shown here. However, in the design of treatment systems the contact time in a reactor is an extremely important consideration. Thus, the comparison here is a valid one.

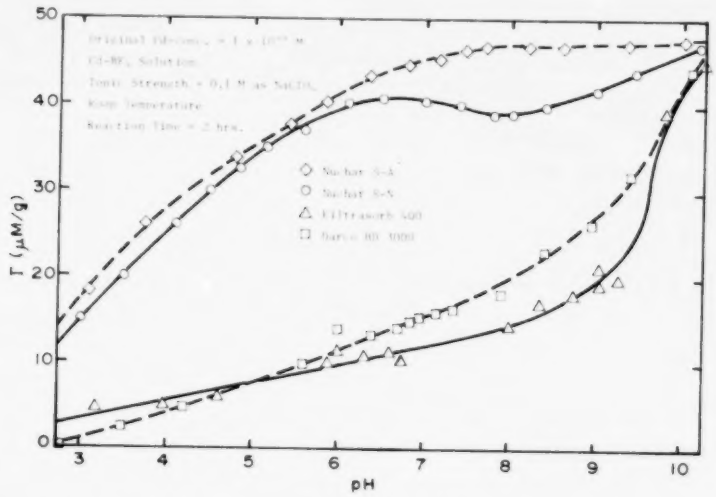


Figure 14. Comparison of Cd(II) adsorption capacity by granular and powdered activated carbon, as affected by pH.

At any rate, the powdered carbons are clearly superior to the granular types for Cd(II) removal. To accurately explain these differences in the adsorptive capabilities requires a thorough understanding of the physico-chemical nature of the individual activated carbons. Mattson and Mark (24) state two general properties which are responsible for the adsorptive nature of carbons. These properties are: (1) the pore-size distribution and surface area of the carbons, and (2) the chemical reactivity of the carbon surface.

Adsorption is a surface phenomenon. Thus, the specific surface area, defined as the portion of the total surface area available for adsorption, is certainly an important factor with respect to the ultimate adsorption capacity. The specific surface area of the powdered carbons is greater than that of the granular carbons, approximately 1.5-2.0 times as much as Filtrasorb 400 and 2.5-3.0 times as great as Darco HD 3000. However, computation of available "parking areas" of the adsorbate Cd(II) molecules reveals that surface area should not be a limiting factor, even for Darco HD 3000, which has the lowest specific surface area of those carbons studied.

For example, consider the experiment involved in producing the results for Figure 14, where the Cd(II) concentration is 10^{-4} moles/ℓ and a 2.0 g/ℓ dose of Darco HD 3000 is added. Using the expression, $\Gamma_m = \Sigma / (N\sigma^o)$, where **Σ is the specific surface area per gram of carbon, N is Avogadro's number, and**

Γ_m is the moles of Cd(II) adsorbed at monolayer coverage per gram of carbon, the area per site, σ^o, can be determined (48). To obtain the most conservative estimate, assume that all of the Cd(II) is adsorbed from solution, that is $\Gamma_m = 5 \times 10^{-5}$ μM/g. Using a value of 600 m^2/g as the specific surface area for Darco HD 3000, one obtains $\sigma^o = 2000$ $Å^2$. An area of 2000 $Å^2$ is certainly adequate for Cd(II) ions, which have a hydrated radius of approximately 3.7 Å. Also, in comparative tests conducted at pH 6 for a 10^{-4} M cadmium wastewater, a 5 g/ℓ dose of Darco HD 3000 did not achieve as great an extent of removal as 1 g/ℓ of either Nuchar SN or Nuchar SA. Thus differences in specific surface area do not entirely account for the varying effectiveness in Cd(II) adsorption for the activated carbons studied.

Another possibility for explaining the differences in adsorption for carbons is the particle size differences. For some granular carbons, the breaking up of a large particle to form smaller ones can in some instances serve to open some tiny, sealed channels in the carbon which then become available for adsorption, thus slightly increasing the adsorption capacity of a given weight of carbon (40). As a result, some batch adsorption experiments were conducted to test this theory. Darco HD 3000 activated carbon was mechanically ground and separated into various sizes. Adsorption data using the ground carbon is reported in Table 8. It indicates that a decrease in particle size does not bring about a substantial increase in Cd(II) adsorption from either the fluoborate or cyanide wastewater solutions.

TABLE 8. Cd(II) Adsorption on Darco HD 3000 Activated Carbon for Various Mesh Sizes.

Solution	pH	Mesh Size*	Size in mm		% Adsorbed
Fluoborate	6.0	4 x 20	4.75	0.84	21.0
		20 x 40	0.84	0.42	21.5
		40 x 70	0.42	0.21	21.8
		70 x 115	0.21	0.14	19.0
		115 x 140	0.14	0.11	22.0
Cyanide	6.5	4 x 20*	4.75	0.84	12.0
		20 x 40	0.84	0.42	12.0
		40 x 70	0.42	0.21	12.4
		70 x 115	0.21	0.14	14.0
		115 x 140	0.14	0.11	12.8

*Mesh size as received.
Experimental Conditions: 1.0 g/ℓ dose; Cd-concentration = 1×10^{-4} M; 0.1 M as $NaClO_4$.

Pore size distribution can also be a determining factor in the adsorption capability of an activated carbon. However, as has already been stated, the hydrated radius of a Cd(II) ion is estimated at 3.7 Å, implying a diameter of 7.4 Å. This is still smaller than the lower value given in the size range for micropores in activated carbons of 10-1000 Å in diameter (47). Therefore, pore size is probably not a critical parameter in terms of equilibrium adsorption capacity for the particular carbons used in this study.

Therefore, for the case of Cd(II) adsorption, it appears that the superiority of the two powdered carbons over the granular brands is due to differences in the chemical reactivity of their surfaces. More specifically, Nuchar SN and Nuchar SA possess certain surface functional groups which readily react with the Cd(II) species in solution, and these groups are not present on the surface of Filtrasorb 400 and Darco HD 3000. The exact nature and characterization of these functional groups is not clearly understood. In their study of Cd(II) adsorption onto activated carbon, Huang and Ostovic (19) cited hydroxo functional groups, formed upon the interaction of the carbon surface with water molecules, as the surface groups responsible for the cadmium adsorption reaction. According to their theory, these hydroxo functional groups serve as a ligand and form metal complexes with the free cadmium ions at the surface of the carbon. However, this is one of several models that have been advanced to explain the adsorption reaction, all of which are regarded as speculative due to the lack of detailed evidence as to the precise nature of the surface functional groups of activated carbon.

Effect of pH on Adsorption

Figures 7 and 14 also illustrate the impact of pH on the extent of Cd(II) adsorption. This influence occurs for several reasons. One is that the distribution of cadmium species is a function of pH. For example, in the cadmium fluoborate system, substantial precipitation of $Cd(OH)_2(s)$ and/or $CdCO_3(s)$ occurs starting at pH 9-10 (Fig. 4). The formation of these species obviously enhances Cd(II) removal at the more alkaline pH values. In fact, the adsorption curves shown in Figure 14 for Filtrasorb 400 and Darco HD 3000 match up quite well with the precipitation data for this system as presented in Figure 4. This indicates that under the stated conditions, Cd(II) removal is due almost exclusively to precipitation at pH values greater than 9.5 for the granular carbons. Whether or not these precipitates are attached to the carbon particulates is unknown, but it is clear that the mechanism for this increase in removal is precipitation. This is further illustrated by the adsorption curve for Nuchar SN. Notice that there is a peak at approximately pH 6.7, followed by a decrease in adsorption. However, the amount removed begins to increase again at pH > 8 due to the ensuing precipitation of cadmium from solution.

Figures 15a and 15b depict adsorption as a function of pH and initial cadmium concentration for Nuchar SN and Nuchar SA in a fluoborate solution. The curves for these two carbons are almost identical, showing nearly linear increase in adsorption density as a function of pH when the pH is less than 7. The removal then approaches a maximum value (e.g., for Cd-concentration = 2×10^{-4} M, Γ_{max} = 100 μM/g), and proceeds to level off at this amount for alkaline pH values due to precipitation. This precipitation effect is more evident for those cases in which the original Cd(II) concentration is highest, with a slight jump occuring between pH 6 and 7. The pH value for the onset of this jump decreases with increasing Cd(II) concentration, which is what would be expected based upon $Cd(OH)_2(s)$ and $CdCO_3(s)$ solubility calculations (Figures 2 and 3).

The distribution of cadmium species as a function of pH for the cyanide system has been illustrated previously (Figure 3b). When this is compared

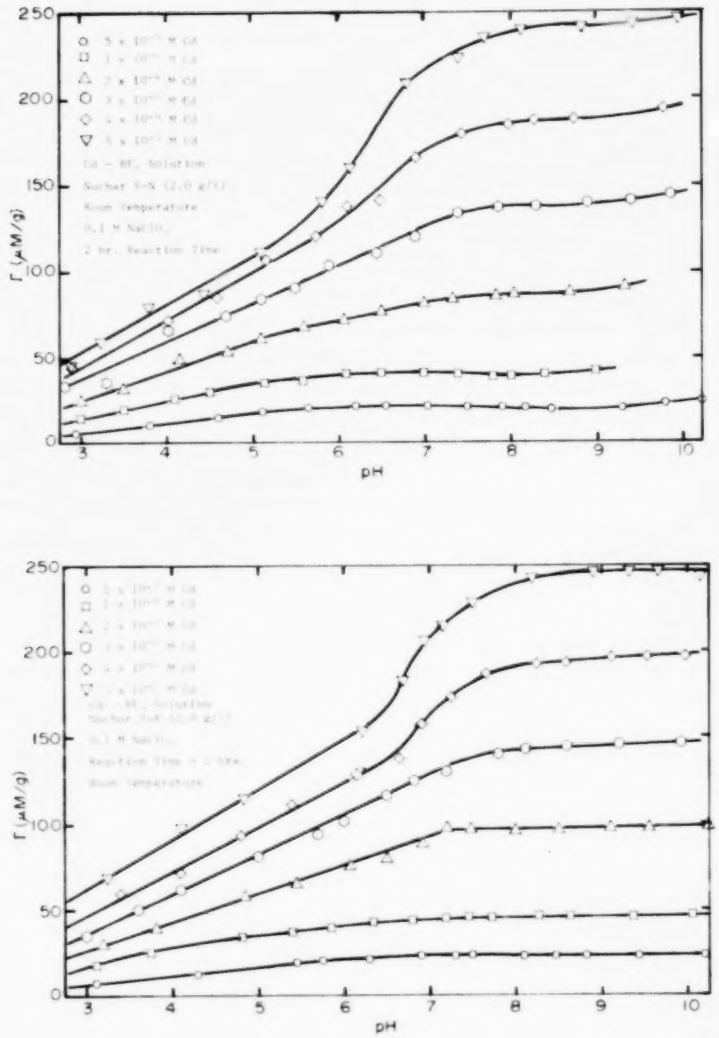


Figure 15. Adsorption characteristics of Cd(II) from synthetic Cd(II)-plating wastewaters ($Cd\text{-}BF_4$ solution) as affected by pH.

with adsorption data for the cadmium cyanide wastewater, it becomes obvious that the pH-dependent speciation plays a significant role in the extent of adsorption. Figure 16 depicts Cd(II) adsorption from a cyanide solution as a function of pH for various initial cadmium concentrations. In contrast to the curves for the fluoborate solution, which show increasing adsorption with increasing pH at nearly every point over the entire pH range, the adsorption density for each of these curves reaches a peak between pH 6 and 7, and then drops off to approximately 30 μM/g at pH 8, regardless of the initial cadmium concentration. However, close examination of the case where the

Cd(II) concentration is 10^{-4} M reveals that the adsorption curve for Nuchar SN peaks at approximately pH 6.6, which is very close to that observed for Nuchar SN in the fluoborate system. The difference in the cyanide solution is, of course, that nearly all of the Cd(II) is complexed with cyanide at pH values greater than 7. As a result, there is no enhancement of cadmium removal due to hydroxide or carbonate precipitation.

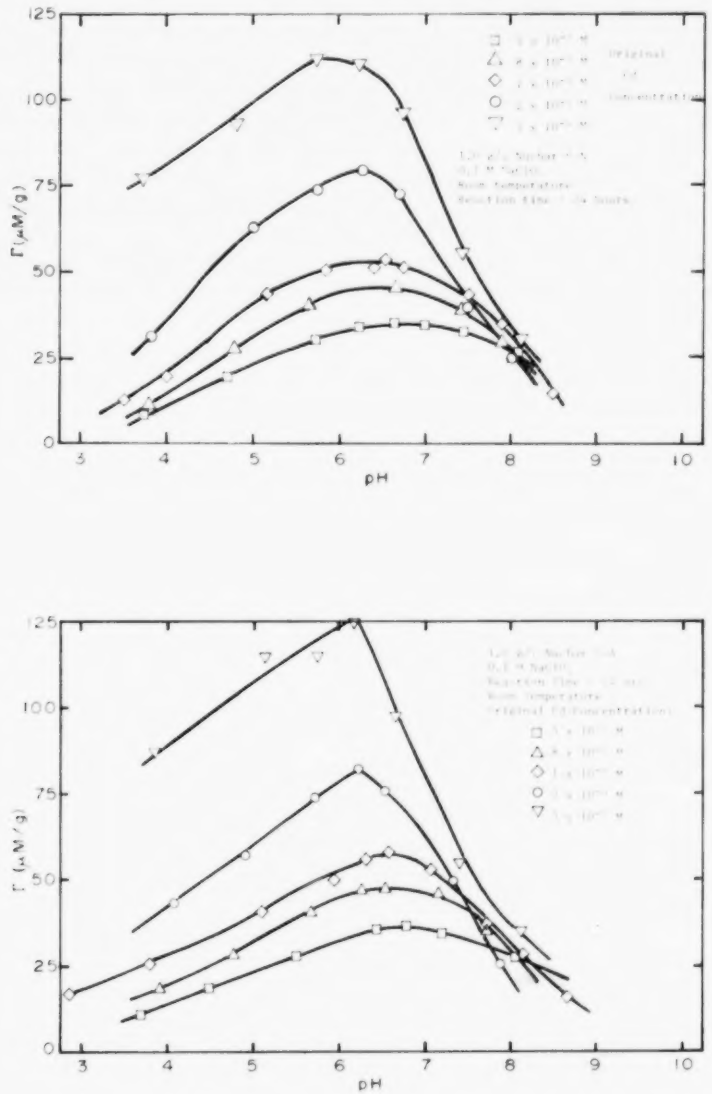


Figure 16. Adsorption characteristics of Cd(II) from synthetic Cd(II)-plating wastewaters (Cd-CN solution) as affected by pH.

This pH effect on Cd(II) adsorption can also be attributed to electrostatic attraction. This in turn is a function of the charge of both the solid adsorbent, in this case activated carbon, and the adsorbate. The charge on the solid is sensitive to the composition of solution, and frequently it is possible to identify certain ionic species as being primarily responsible for the surface charge (49). Huang and Ostovic (19) demonstrated that H^+ and OH^- are the surface potential determining ions for hydrous carbons, indicating the pH dependence of surface charge. A point of zero net charge, or pH_{zpc}, has been determined for Nuchar SA as 3.80, and 5.84 for Nuchar SN. At $pH < pH_{zpc}$, it is negative. As has already been seen, the distribution of cadmium cyanide species is also a function of pH, with negatively charged $Cd(CN)_3^-$ and $Cd(CN)_4^{-2}$ most prevalent at pH > 8. At these values, then, an unfavorable condition of electrostatics exists, with both the carbon and cadmium species possessing negative charges. This electrostatic repulsion helps to account for the sharp decrease in adsorption as shown in the curves for the cyanide system, and demonstrates more fully the impact of solution pH on adsorption.

Figure 15 illustrates still another means by which pH affects adsorption. Notice that for pH values greater than 7, any two curves are nearly equidistant from each other. In contrast, the curves begin to converge for decreasing pH at pH values less than 7, with the slopes of the curves increasing for increasing cadmium concentration. These trends suggest that hydrogen ions (H^+) are being adsorbed onto the carbon, and therefore are competing with the Cd^{+2} ions for adsorption sites on the carbon surface. This explains, at least in part, the decrease in cadmium adsorption for increasing hydrogen ion concentration. When the cadmium concentration is increased, the ratio of Cd^{+2} ions to H^+ ions becomes greater. As a result, Cd^{+2} is more "competitive" for the available sites, thus explaining the increase in slope for increasing adsorbate concentration.

The adsorption-pH curves for cadmium cyanide demonstrate this same idea for the region to the left of the peak. In this case, though, the exact opposite effect is occuring to the right of the peak, with the curves converging even more dramatically. This may be influenced, in part, by the fact that activated carbons are also known to adsorb hydroxide ions quite strongly, with a resulting "competitive" effect. However, such a steep decrease is probably due to the ideas previously mentioned; these being the absence of precipitation enhancement and the unfavorable electrostatic condition, both brought about by the pH-controlled cadmium cyanide complex formation.

Effect of Carbon/Cd(II) Concentration-Adsorption Isotherms

Figures 15 and 16 also illustrate the effect of initial Cd(II) concentration on adsorption. Increasing the adsorbate concentration increases the adsorption density over the entire pH range considered, the only exception being adsorption from the cyanide solution when the pH > 8. As mentioned in the previous section, this is especially important for acidic pH values, for it is in this region where the Cd^{+2} ions must compete with H^+ ions for the available sites on the carbon surface. Also cited previously was the fact that precipitation begins to enhance adsorption at a lower pH value for increasing Cd(II) concentration in the fluoborate solution. Similarly, the adsorption peak for the cyanide system shifts slightly from right to left when

the initial adsorbate concentration is increased. This shift can be described in terms of speciation and electrostatic interactions. For instance, when the Cd(II) concentration is 5×10^{-4} M, the total cyanide concentration is 5×10^{-3} M. Stability calculations using these values show that the Cd-CN speciation distribution also shifts slightly from right to left (note the dashed line for the Cd^{+2} species in Figure 4). With the various cadmium cyanide complexes also forming at a lower pH value, including the negatively charged $Cd(CN)_3^-$ and $Cd(CN)_4^{-2}$ species, it follows that the unfavorable electrostatic condition, spoken of in the previous discussion, will begin to prevail at a lower pH, thus accounting for the observed shift.

Figure 17 presents data obtained for a different approach. In this case, the carbon dose was varied for the same initial Cd(II) concentration. This diagram is beneficial in giving a clearer picture of possible optimum conditions for adsorption, in this case, from the fluoborate solution using Nuchar SN. For example, 85 percent Cd(II) removal is achieved at pH 7 when the carbon/cadmium ratio is 0.250 g/mg (carbon dose - 2.81 g/ℓ). However, 77 percent removal can be attained by adding just 1.0 g/ℓ (C/Cd = 0.89 g/mg), and adjusting the pH to 7. Perhaps a better choice still would be to add 2.81 g/ℓ of Nuchar SN (C/Cd = 0.250 g/mg), keeping in mind that the solution-pH upon addition of the carbon is about 6.10. This alternative would require little or no pH adjustment for treatment, certainly advantageous from an economic standpoint.

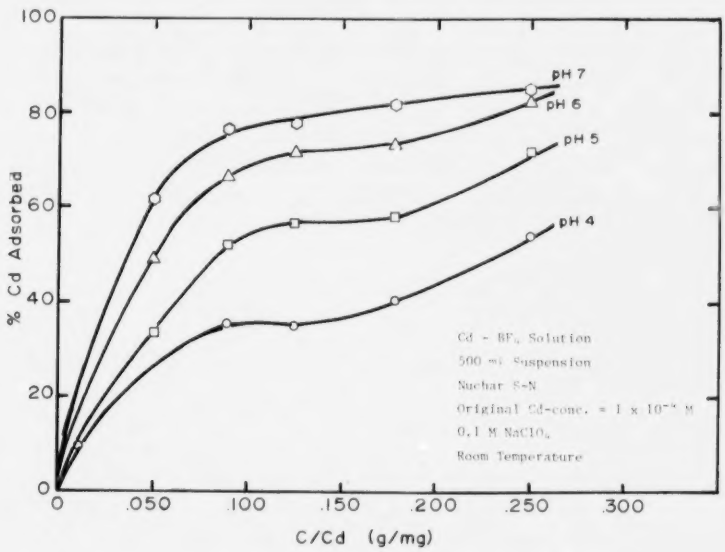


Figure 17. Extent of Cd(II) adsorption as affected by carbon/cadmium ratio at various pH.

Data from Figures 15-17 were used to obtain adsorption isotherms. The adsorption isotherm expresses the specific relationship between the concentration of adsorbate and its degree of removal from solution by an adsorbent

at constant temperature (40). Figure 18a displays this relationship for Cd(II) from the fluoborate solution when Nuchar SA is the adsorbent. Since pH is such a critical parameter for adsorption, unique isotherms have been determined for various pH values. The original Cd(II) concentration range for this figure is 5×10^{-5} M to 5×10^{-3} M. One noticable feature here is the large gap between the pH 6 and pH 7 isotherms, particularly in the high concentration range. This is a result of the significant enhancement of Cd(II) removal brought about by precipitation at the higher pH values. Thus the data points for the upper portion of the pH 7 and pH 8 isotherms may or may not reflect true adsorption density. Precipitation may also account for the slight "take off" in the pH 6 isotherm at high equilibrium concentrations of cadmium.

Figure 18b gives adsorption isotherms for cadmium removal from the cyanide solution using Nuchar SN as the adsorbent. The curves for the pH range 4-6 are similar to those for the fluoborate system in that adsorption increases roughly at the same rate with increasing adsorbate concentration. However, the pH 7 isotherm transverses the others, demonstrating a decrease in adsorption at this pH value, particularly for higher adsorbate concentrations.

Actually, only the beginning portion of the isotherm is of practical interest, since the cadmium concentrations here are equivalent to those found in actual plating wastewaters. The initial portion of the pH 6 isotherm for the Nuchar SA, Cd-BF_4 system is shown in Figure 18c and compared with one for cyanide. Also pictured are comparable isotherms for adsorption using Darco HD 3000, a granular carbon. Not only does this point out, once again, the

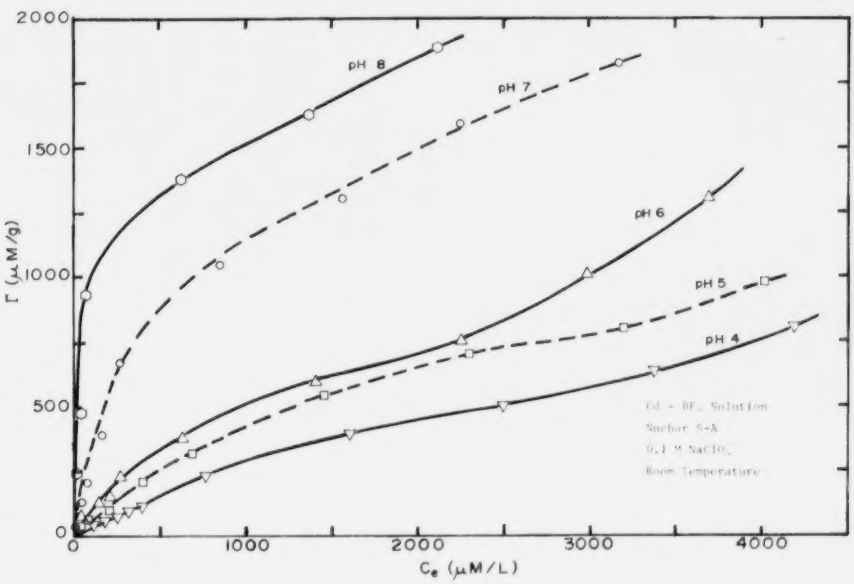


Figure 18a. Adsorption isotherms of Cd-BF_4 solution as Nuchar SA.

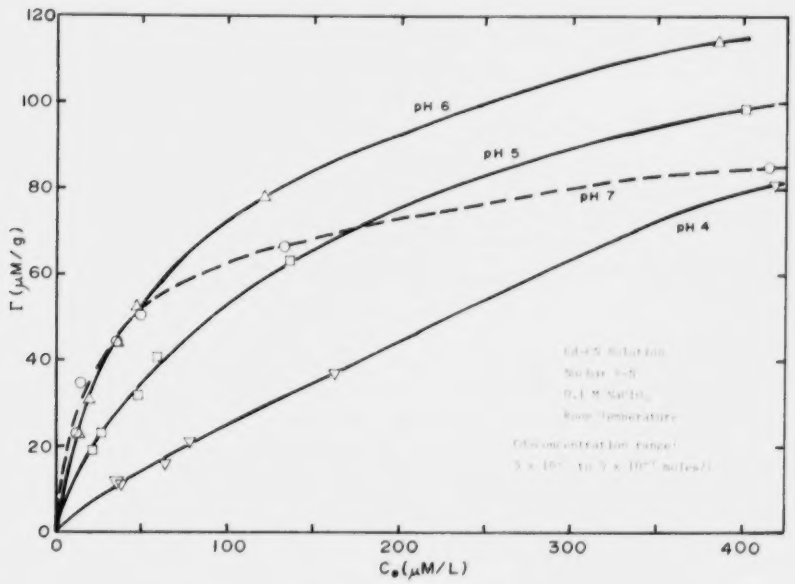


Figure 18b. Adsorption isotherms of Cd-CN solution on Nuchar SN.

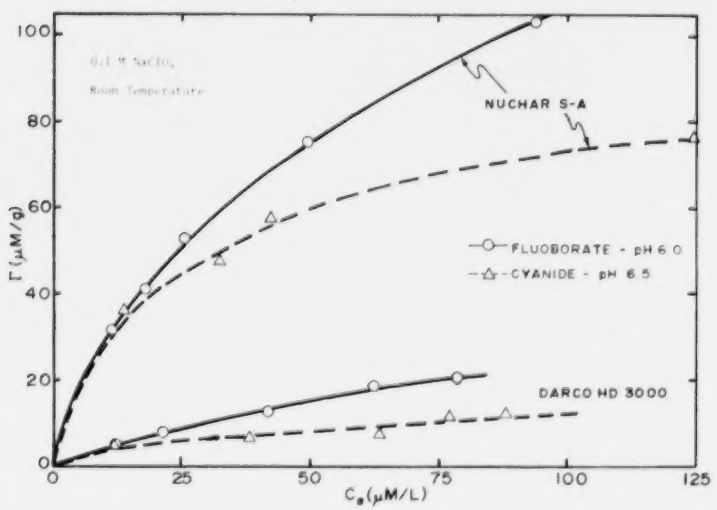


Figure 18c. Typical adsorption isotherm-comparison of various systems. Removal efficiency is generally better with $Cd\text{-}BF_4$ than Cd-CN solution.

superiority of the powdered carbons for cadmium removal, but it also demonstrates that cadmium is adsorbed at a slightly higher density from the fluoborate solution than from the cyanide system. There are several factors that may account for this difference. One is that at higher pH values (pH > 6.5), the electrostatic conditions are unfavorable for adsorption in the cyanide solution. Another is that, in the cyanide solution, the molar ratio of CN:Cd(II) is 10:1, while in the fluoborate solution, the ratio of BF_4:Cd(II) is only 2.7:1. Huang (50) cited Bernardin, who reported that cyanide was removed from wastewater by adsorption on activated carbon, and in fact became oxidized at the adsorption sites in the presence of metal and O_2. Huang and Wu (43) also reported significant cyanide adsorption onto activated carbon. With such a large excess of cyanide in solution, as compared to fluoborate, it is likely that cyanide competes with cadmium for adsorption sites, so that reducing the CN:Cd(II) ratio would increase Cd(II) adsorption. It should be noted that cyanide adsorption by activated carbon, and detoxification, as a result of site oxidation to CNO^-, is extremely important, since CN^- is also a toxic pollutant which must be removed from electroplating wastewaters.

The adsorption isotherm is a useful starting point in the development of mathematical expressions to model the extent of adsorption from solution. Two of the more commonly used adsorption relationships will be discussed here in conjunction with the experimental data; they are the Langmuir and Freundlich isotherms. The Langmuir model can be derived from either kinetic, statistical, or thermodynamic considerations, while only statistical and thermodynamic derivations exist for the Freundlich expression. All of these derivations are readily available in the literature (48,51,52).

The Langmuir isotherm can be conveniently expressed in linear form as:

$$\frac{1}{\Gamma} = \frac{1}{\Gamma_m} + \frac{1}{b_m}\left(\frac{1}{C_e}\right) \qquad (1)$$

where C_e is the equilibrium Cd(II) concentration in solution (μmoles/ℓ), Γ is the amount of cadmium adsorbed at concentration C_e (μmoles/g-carbon), Γ_m is the maximum or limiting adsorption density (μmoles/g-carbon), and b is a constant related to the energy of adsorption. A plot of $1/C_e$ vs. $1/\Gamma$ gives a straight line with a slope of $1/b\Gamma_m$ and an intercept of $1/\Gamma_m$. There are three basic assumptions involved in the Langmuir model. These are: (1) each site can accommodate one and only one adsorbed particle, implying monolayer adsorption; (2) the adsorption is localized, which means that the adsorbed molecules do not migrate about the plane of the surface of the solid; and, (3) homogeneity in the surface, i.e., the energy of an adsorbed particle is the same anywhere on the surface (31,51). Figure 19 gives the linearization of Langmuir adsorption isotherms for both Nuchar SA and Darco HD 3000 for the fluoborate system. The Langmuir constants for the Nuchar SA isotherm are, Γ_m = 162.34 μmoles/g, and b = 0.0196 ℓ/μmole; while for Darco HD 3000 they are, Γ_m = 69.93 μmoles/g, and b = 0.0055 ℓ/μmole. Clearly, Nuchar SA is a more effective adsorbent, as not only is its maximum adsorption capacity much higher than that of Darco, but its b value is substantially greater, indicating a greater tendency towards adsorption in this system.

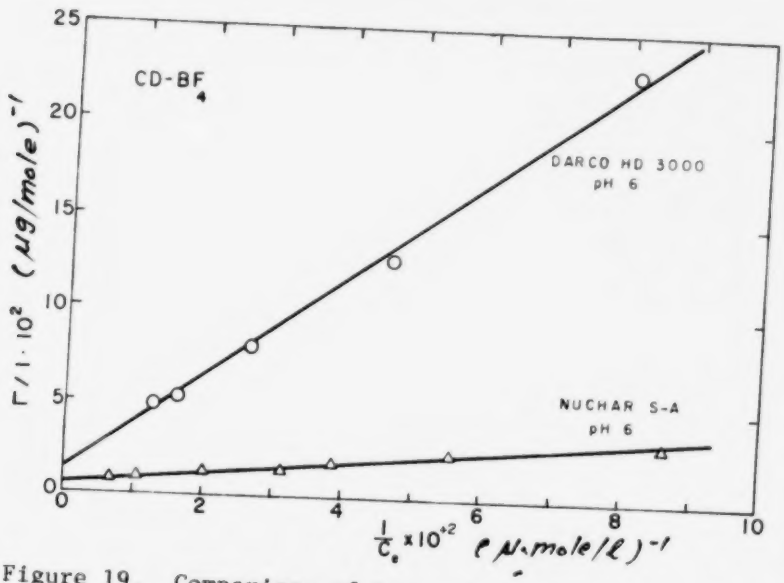


Figure 19. Comparison of Langmuir linearization of adsorption isotherms from $Cd-BF_4$ solution.

One of the necessary conditions for the validity of an adsorption theory is that it accurately describe the experimental data. This appears to be the case for the Langmuir model, at least for the concentration range of major interest (original Cd(II) concentration of 5×10^{-5} M to 5×10^{-4} M). Although it is doubtful that the assumptions given for the development of the Langmuir model are precisely met, this treatment serves as a useful mathematical descriptor of the equilibrium data. The parameters, Γ_m and b, quantify the limiting capacity for adsorption and the intensity of adsorption respectively. This permits meaningful quantitative comparison of adsorption behavior in different carbon-cadmium systems, or for varying conditions within any given system, such as a change in pH (47).

The general form of the Freundlich isotherms is:

$$\Gamma = KC_e^n \qquad (2)$$

where K and n are constants ($n < 1$), and Γ and C_e are as described for the Langmuir model. This equation can be linearized to the following:

$$\log \Gamma = \log K + n \log C_e \qquad (3)$$

By plotting log Γ vs. log C_e, the constants can be obtained from the intercept, which is log K, and the slope, which is equal to n. Figure 20 depicts the linearized Freundlich isotherms for cadmium adsorption from the fluoborate solution using Nuchar SA and Nuchar SN respectively.

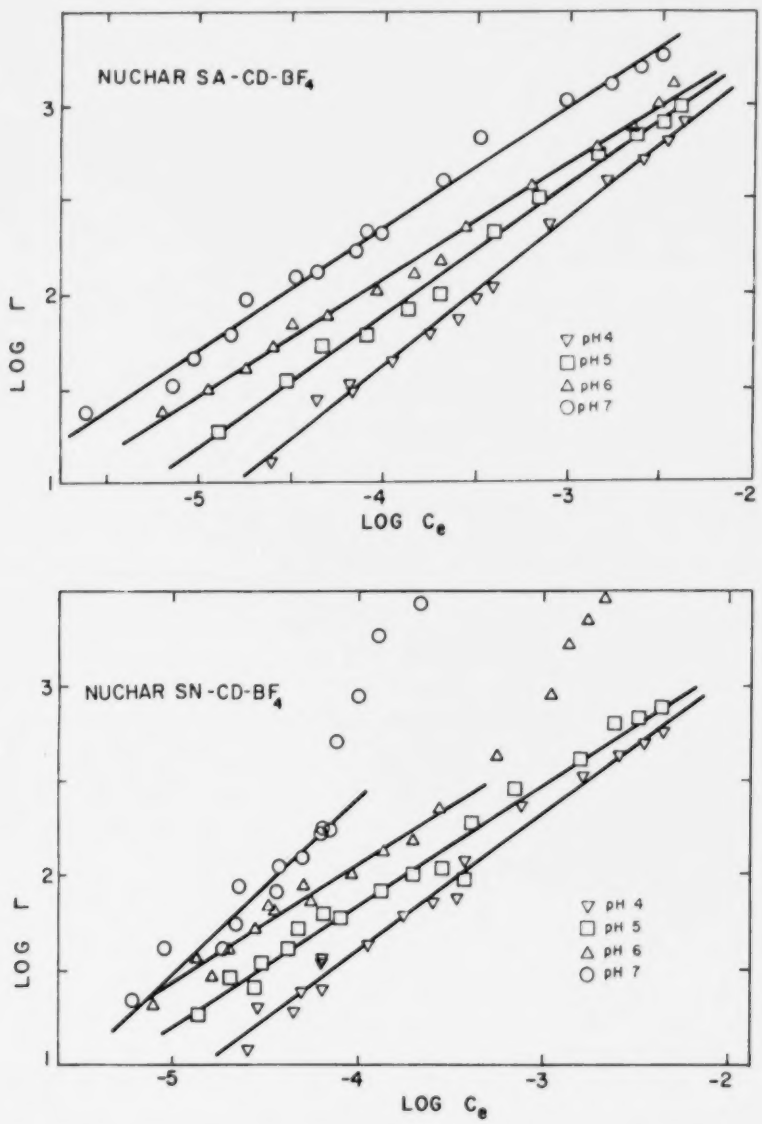


Figure 20. Freundlich linearization of adsorption isotherms at various pH values for Cd-BF_4 solution (a) on Nuchar SA (top); (b) on Nuchar SN (bottom).

This model appears to provide an excellent fit for the experimental data for the case where Nuchar SA is used as the adsorbent. The data points cover an initial Cd(II) concentration range of 5×10^{-5} M to 5×10^{-3} M. For the fluoborate-Nuchar SN system, the fit is not nearly as satisfactory, particularly at pH 6 and pH 7. At these values, the linearization can only be approximated for a Cd(II) concentration range of 5×10^{-5} M to 5×10^{-4} M. The constants, K and n, have been determined for these two systems and are presented in Table 9.

TABLE 9. Empirical Constants for Freundlich Adsorption Isotherms.*

Carbon Carbon	pH	Cd(II) Concentration Range	Slope = n	Log K
Nuchar SA	4	$5 \times 10^{-5} - 5 \times 10^{-3}$ M	0.779	4.73
	5	$5 \times 10^{-5} - 5 \times 10^{-3}$ M	0.695	4.66
	6	$5 \times 10^{-5} - 5 \times 10^{-3}$ M	0.617	4.54
	7	$5 \times 10^{-5} - 5 \times 10^{-3}$ M	0.643	4.92
Nuchar SN	4	$5 \times 10^{-5} - 5 \times 10^{-3}$ M	0.730	4.52
	5	$5 \times 10^{-5} - 5 \times 10^{-3}$ M	0.644	4.41
	6	$5 \times 10^{-5} - 5 \times 10^{-4}$ M	0.622	4.54
	7	$5 \times 10^{-5} - 5 \times 10^{-4}$ M	0.933	6.14

*Data are shown in Figure 20.

Modified Langmuir Adsorption Model

The double reciprocal plots in Figure 19 suggest that the equilibrium adsorption data can be adequately described by the Langmuir equation. Figure 19, which is a double reciprocal plot for one of the experimental systems at several pH values, appears to provide further verification of this point. In all cases the isotherms were statistically fitted to the experimental results using least squares linear regression analysis.

Figures 21-24 show clearly that the hydrogen ion concentration exhibits a major effect on the extent of cadmium adsorption. In an attempt to quantify these effects, three variations of the Langmuir isotherm were examined. These are the same variations that have been used to model enzyme kinetics, and thus may be useful in helping to describe the seemingly "inhibitory" effect of increasing hydrogen ion concentration on adsorption over the pH range of interest (pH 4-7) (53). These three variations, namely competitive, uncompetitive, and noncompetitive inhibition are described below and illustrated in Figure 25.

Competitive model--According to the competitive model, the proton ions interact directly with the carbon surface, competing with Cd(II) ions for the available sites (Fig. 25). As given previously, the general form of the Langmuir linearization is:

$$\frac{1}{\Gamma} = \frac{1}{\Gamma_m} + \frac{K_m}{\Gamma_m}\left(\frac{1}{C_e}\right) \qquad (4)$$

where the constant b in Equation (1) has now been substituted by $1/K_m$. For the competitive isotherm, the intercept term, $1/\Gamma_m$, remains constant, but the slope term needs to be modified by $1 + [H^+]/K_i$ to include the effect of changing pH. Thus Equation (4) becomes the following:

$$\frac{1}{\Gamma} = \frac{1}{\Gamma_m} + \frac{K_m}{\Gamma_m}\left(1 + \frac{[H^+]}{K_i}\right)\frac{1}{C_e} \qquad (5)$$

where Γ, Γ_m, and C_e are as described previously, $[H^+]$ is hydrogen ion concentration, K_m is the rate constant for the C-Cd(II) complex formation reaction, and K_i is the rate constant for the C-H^+ complex formation reaction.

Uncompetitive model--For uncompetitive inhibition the proton ions do not react with the carbon surface directly, but instead react with the carbon-cadmium complexes (Fig. 25). In this case, the slope term of the Langmuir linearization remains unchanged, and the intercept is modified to become:

$$\frac{1}{\Gamma} = \frac{1}{\Gamma_m}\left(1 + \frac{[H^+]}{K_i}\right) + \frac{K_m}{\Gamma_m}\frac{1}{C_e} \qquad (6)$$

where K_i is now the rate constant for the C-Cd(II)-H^+ complex formation reaction.

Noncompetitive model--This mechanism is a combination of the first two. Both the Cd(II) and H^+ ions adsorb independently at different sites on the carbon surface (Fig. 25). In other words, H^+ ions react with both carbon sites and C-Cd(II) complex, while Cd(II) ions react with carbon sites and C-H^+ complexes (53). In this case, Equation (4) is not expressed as:

$$\frac{1}{\Gamma} = \left(\frac{1}{\Gamma_m} + \frac{K_m}{\Gamma_m}\frac{1}{C_e}\right)\left(1 + \frac{[H^+]}{K_i}\right) \qquad (7)$$

In examining the reciprocal plot of Figures 21-24, it appears that the hydrogen ion acts as a competitive inhibitor, at least over the pH range of 4-6. The constants, K_m and K_i, can be determined by plotting the slopes of the lines of the double reciprocal plot versus the hydrogen ion concentration. Such a plot is shown in Figures 21-24, where the slopes of the double reciprocal isotherms are given as $K_{m\ app}/\Gamma_m$. This same competitive inhibition tendency was seen to exist in cadmium adsorption from both the fluoborate and cyanide solutions, and for both Nuchar SA and Nuchar SN. Double reciprocal plots as well as slope versus $[H^+]$ replots for each of the four experimental systems are given in Fig. 21-24.

The values of the constants, Γ_m, K_m, and K_i, are tabulated in Table 10. Also included are the Langmuir constants for the pH 7 isotherms. At pH 7, the hydrogen ion concentration is becoming so small that its effect is more like that of a noncompetitive inhibitor in the fluoborate system, and an uncompetitive one in cyanide solutions. In addition, other factors such as precipitation begin to play a role in cadmium removal at pH > 7, making application of this model more difficult. However, generally speaking, the modified Langmuir model affords an accurate mathematical description of the extent of cadmium adsorption over the given pH range.

Effect of Ionic Strength

Figures 26 and 27 show the influence of ionic strength on the adsorption

TABLE 10. Constants for Competitive Langmuir Adsorption Model.

System	Γ_m (μ moles/g)	K_m*(μ moles/ℓ)	K_i (μ moles/ℓ)
Nuchar SA:			
$Cd-BF_4$	162.3	68.2	28.8
Cd-CN	115.3	75.2	35.4
Nuchar SN:			
$Cd-BF_4$	182.8	110.2	39.4
Cd-CN	119.0	77.1	25.5
pH 7 Isotherms:			
Nuchar SA:			
$Cd-BF_4$	400.7	77.5*	
Cd-CN	72.2	16.2*	
Nuchar SN:			
$Cd-BF_4$	850.6	284.5*	
Cd-CN	93.3	42.8*	

*K_m = 1/b in Equation (2).
Experimental Conditions: Cd-concentration range = 5×10^{-5} M to 5×10^{-4} M; pH range = 4 - 6; Ionic strength = 0.1 M as $NaClO_4$; Room temperature = 26±1°C.

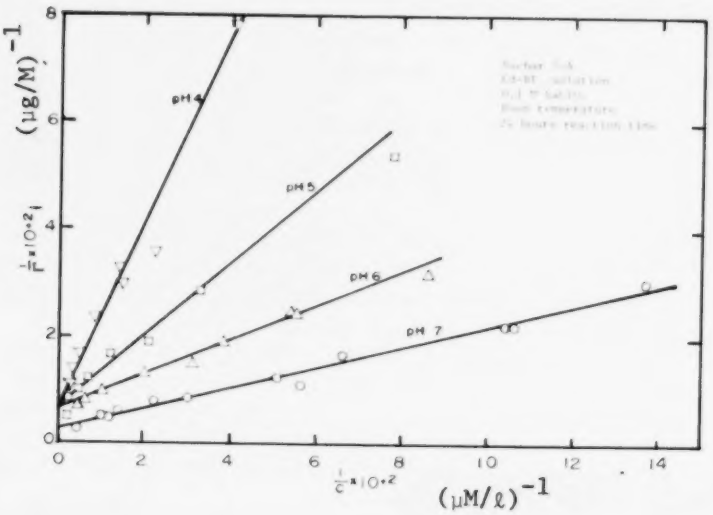
of cadmium onto activated carbon. Data were obtained for five different molar concentrations of background electrolyte, ranging from 0.01 M to 1.0 M, and at two pH values for each system studied. The results indicate that Cd(II) uptake decreases for increasing ionic strength, I. Plotting the adsorption density against the log of the reciprocal of I (or -log I) gives a linear approximation of the relationship between cadmium removal and ionic strength.

That the extent of adsorption is sensitive to changes in concentration of supporting electrolyte indicates that electrostatic attraction may be a significant component of the overall adsorption in this system. The electrostatic free energy, G_{elect}, contributes to the total free energy of adsorption, ΔG_{ads}, and depends on the ionic strength of solution (49,54). This term is given as:

$$\Delta G_{elect} = zF\psi_d \qquad (8)$$

where Z is the ionic charge, F is the Faraday constant, and ψ_d is the potential in the plane of the adsorbing ion (49).

When the ionic strength is increased, the electrical double layer around the adsorbate cadmium ion is compressed, which leads to a decrease in the electrostatic potential, ψ_d (54). The result is a reduction in the coulombic free energy, and consequently, a decrease in cadmium adsorption.



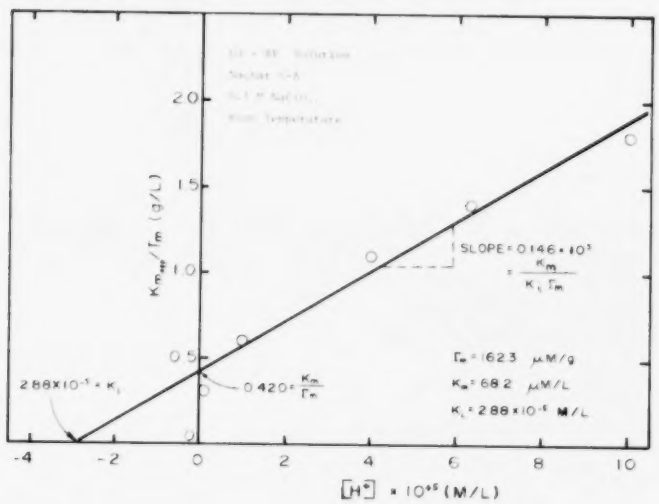


Figure 21. Linearized Langmuir plots and plots to obtain K_i (for pH). Cd-BF_4 solution and Nuchar SA.

Electrostatic adsorption has already been shown to offer a substantial contribution to the total adsorption reaction. This may also help to explain some of the other trends exhibited by the experimental data. One such trend is that in every case, the slope is slightly greater for the higher pH value (6.0 for the fluoborate solution and 6.5 for cyanide). This may be explained by the fact that the coulombic interactions will be greater at these higher pH values. For example, for Nuchar SN, the pH_{zpc} value defines a negative charge on the carbon surface at pH 6 and a positive surface at pH 4 for the adsorption of Cd^{+2} ions. The pH_{zpc} of Nuchar SA is 3.80, signifying a negative

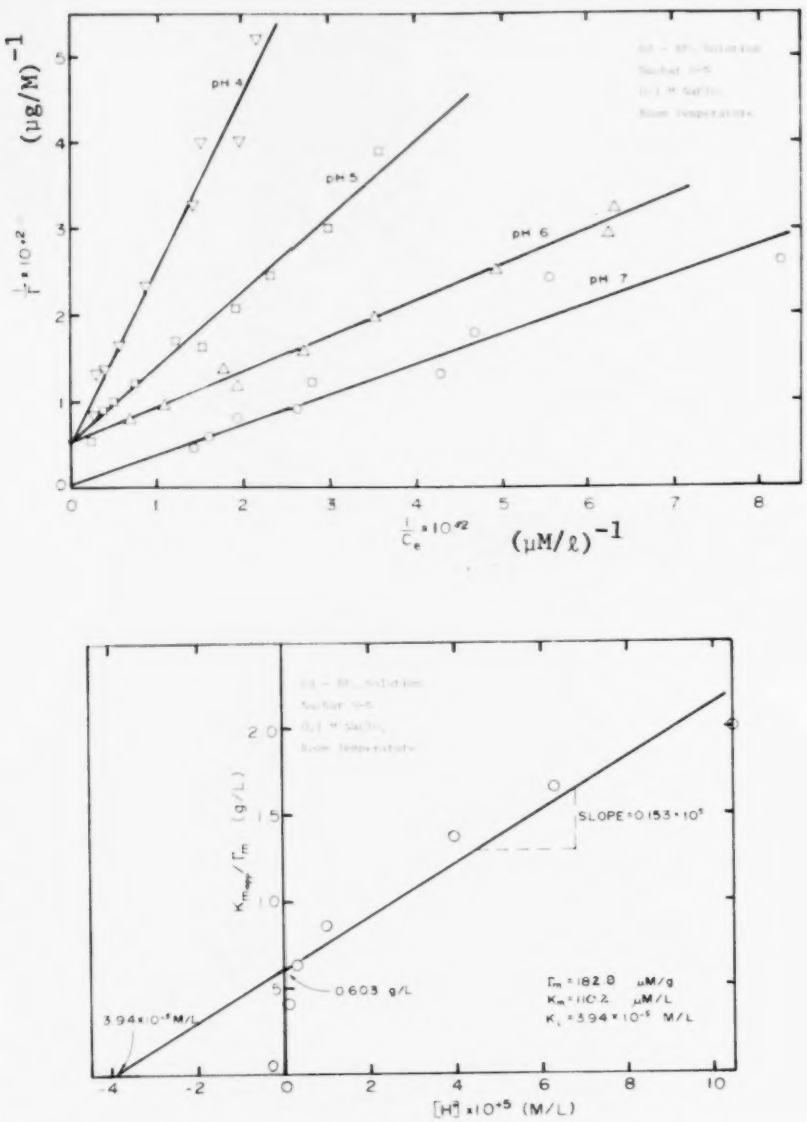


Figure 22. Linearized Langmuir plots and plots to obtain K_i (for pH). Cd-BF_4 solution and Nuchar SN.

surface charge at both pH values for the adsorption of the Cd^{+2} cation. However, the Nernst equation shows that ΔG_{elect} will be greater for the higher pH values; hence, this may explain the "steeper" slopes for these cases. This same idea may also explain why the slopes of the Γ vs. -log I curves are steeper for Nuchar SA than for Nuchar SN. Because of its lower pH_{zpc}, the electrostatic free energy in the Nuchar SA systems will be larger for the particular pH values considered, which suggests that these cases would be more sensitive to changes in background electrolyte concentration.

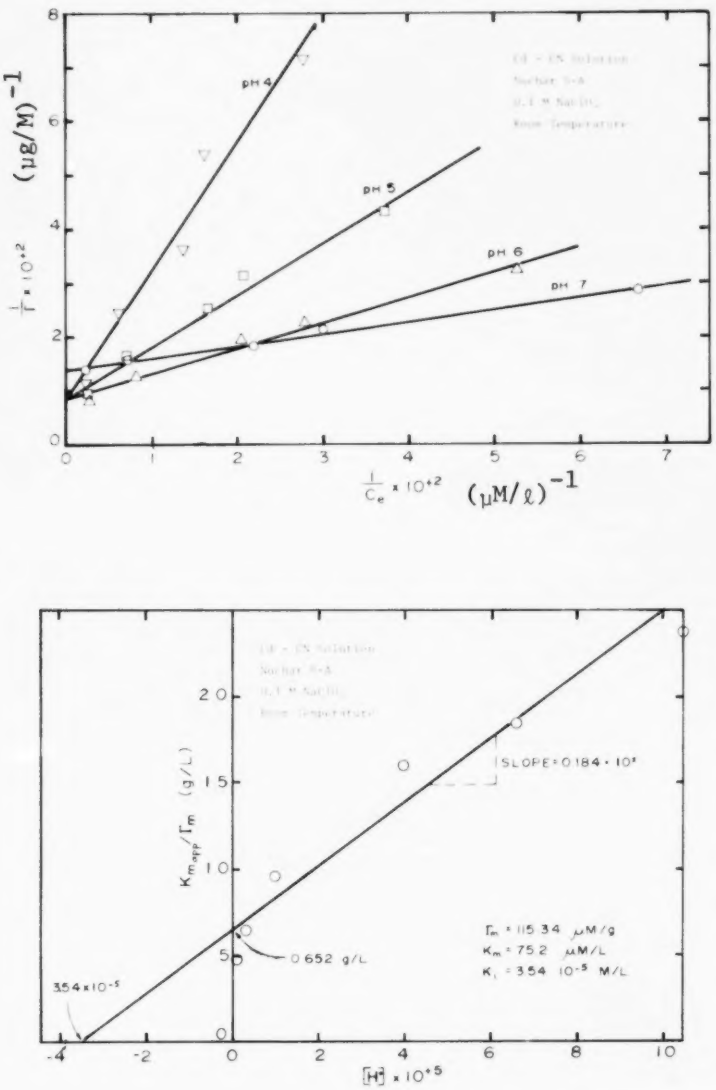


Figure 23. Linearized Langmuir plots and plots to obtain K_i (for pH). Cd-CN solution and Nuchar SA.

Although ionic strength effects were tested for only two pH values in each system, it is still reasonable, based upon the experimental data, to conclude that a decrease in supporting electrolyte concentration leads to an increase in the adsorption of Cd(II) from electroplating wastewaters. In all of the kinetics and equilibrium studies, an ionic strength of 0.1 M was used. This value would be considered as high for most cadmium industrial wastewaters. Hence, the adsorption results could be labelled as "conservative" when making considerations for actual design.

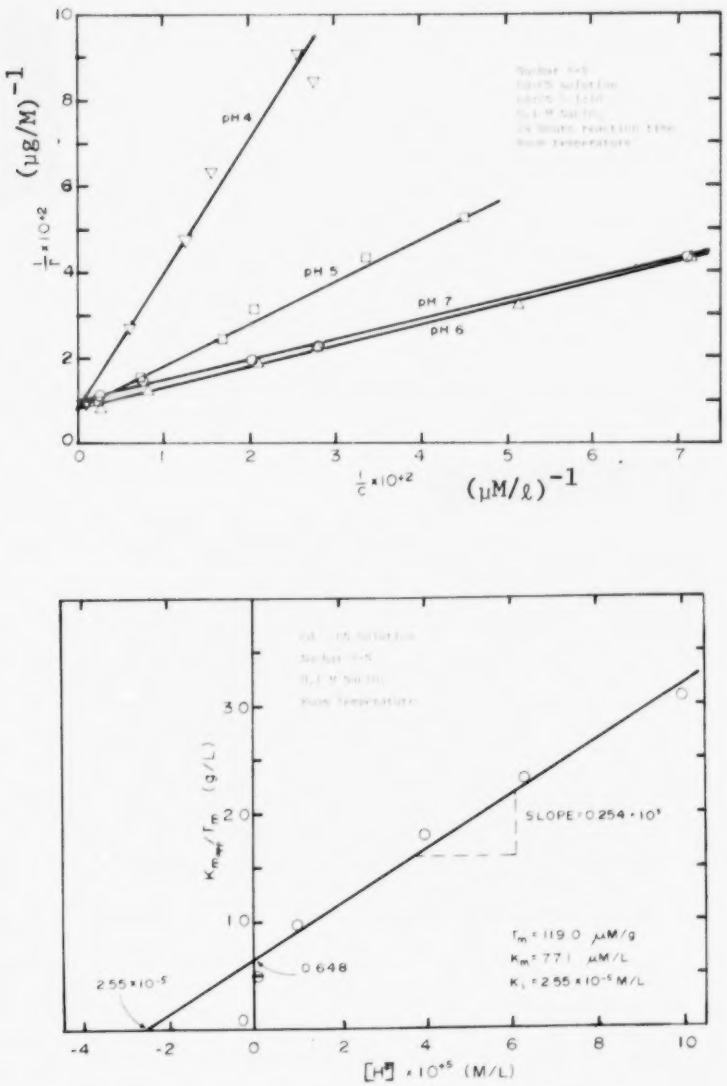


Figure 24. Linearized Langmuir plots and plots to obtain K_i (for pH). Cd-CN solution and Nuchar SN.

Effect of Temperature

The temperature dependence of Cd(II) adsorption onto activated carbon is demonstrated in Table 11. The results show that, in general, adsorption increases for an increase in temperature. This increase was most dramatic at the more acidic pH values, while only small changes in the amount adsorbed were observed at pH 6 and 6.5 for the fluoborate and cyanide systems, respectively.

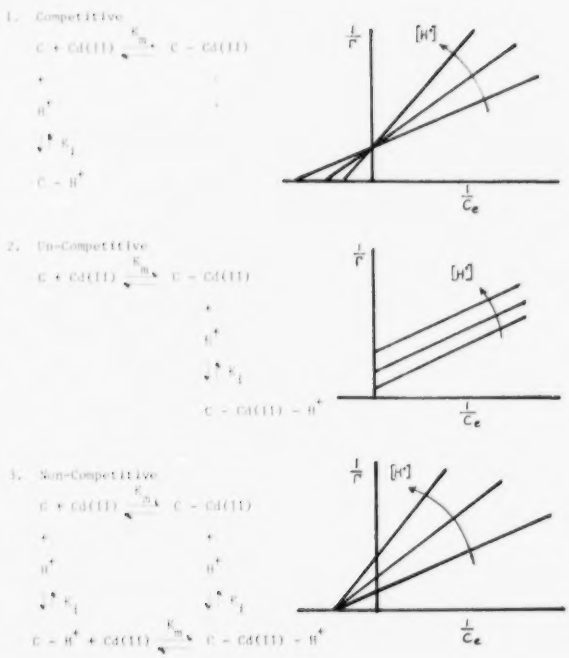


Figure 25. Schematic of variations of Langmuir adsorption isotherms.

TABLE 11. Effect of Temperature on Cadmium (II) Adsorption

Carbon Type	pH	% Adsorbed 10°C	26°C	40°C	60°C
Fluoborate Solution:					
Nuchar SN	4	24.0	33.0	33.2	35.9
	6	64.7	65.8	66.2	68.0
	8	78.0	78.2	82.4	84.4
Nuchar SA	4	24.7	32.5	33.3	37.9
	6	62.0	67.6	67.0	70.7
	8	88.2	90.2	91.0	92.4
Cyanide Solution:					
Nuchar SN	4.5	21.2	27.0	32.8	36.2
	6.5	51.3	51.8	52.0	55.7
	8.5	10.8	14.8	15.0	15.5
Nuchar SA	4.5	20.9	27.0	31.6	36.8
	6.5	52.5	52.2	53.0	55.7
	8.5	9.7	12.0	12.8	14.2

Experimental Conditions: Cd(II) Concentration = 1 $x10^{-4}$ M; Ionic Strength = 0.1 M $NaClO_4$; Carbon Dose = 1.0 g/ℓ.

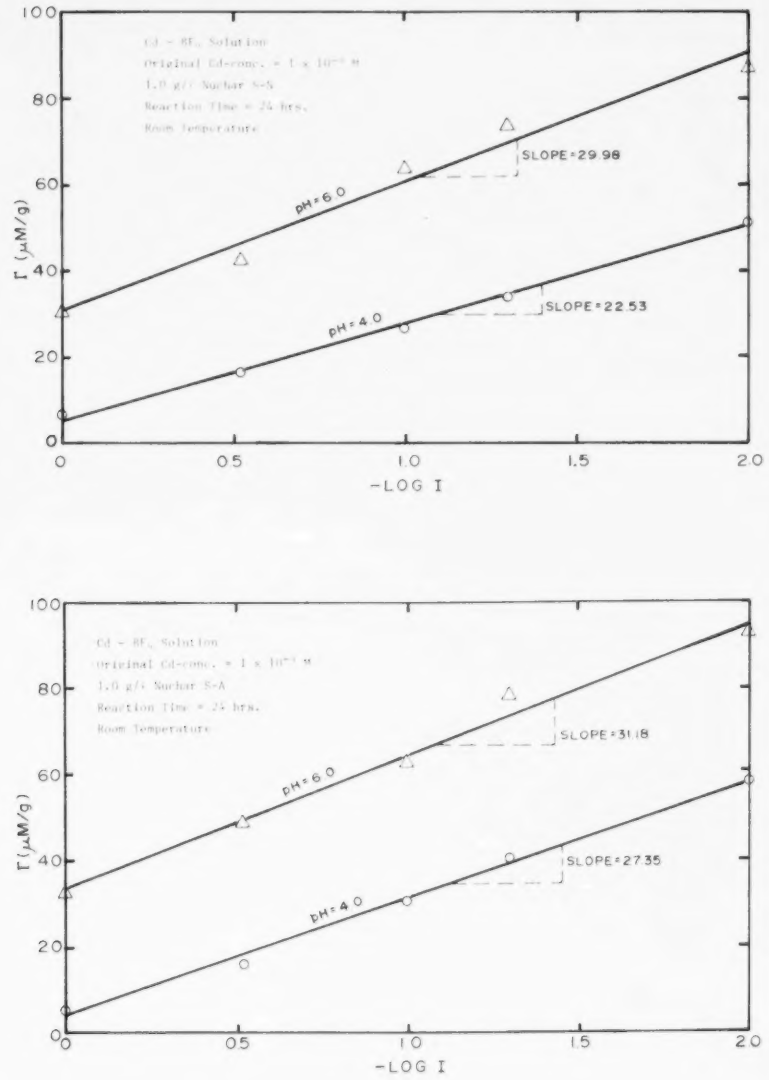
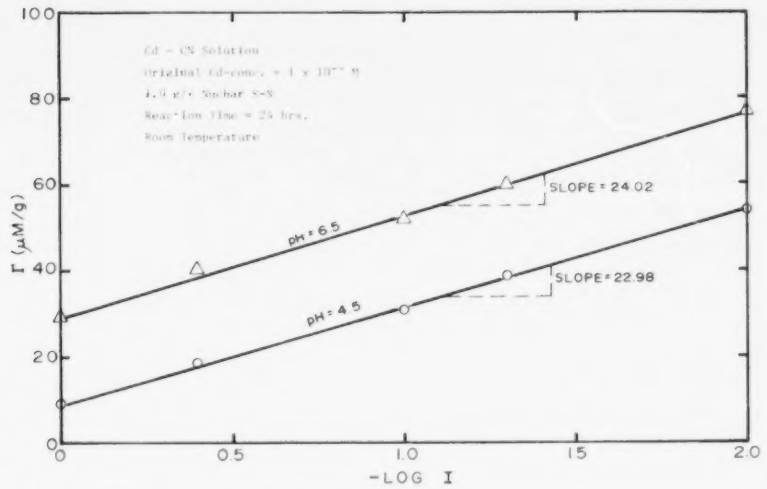


Figure 26. Effect of ionic strength ($NaClO_4$) on Cd(II) removal from Cd-BF_4 solution: (a) Nuchar SN (top); (b) Nuchar SA (bottom).

An increase in adsorption with temperature is unexpected from thermodynamic considerations. Adsorption occurs as a response to a decrease in surface free energy, ΔG, and is also accompanied by a decrease in entropy, ΔS. From the equation:

$$\Delta G = \Delta H - T\Delta S \qquad (9)$$



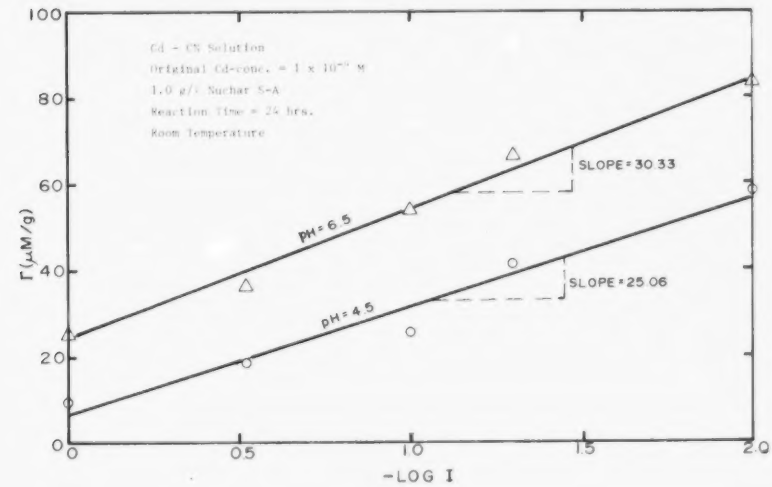


Figure 27. Effect of ionic strength ($NaClO_4$) on Cd(II) removal from Cd-CN solution: (a) Nuchar SN (top); (b) Nuchar SA (bottom).

ΔH must decrease. In other words, adsorption is always exothermic (48). Therefore, the increase in removal must arise from extrinsic processes which are altered by increases in temperature.

For example, temperature changes may affect the competition between Cd^{+2} and H^{+} ions. If ΔH for the formation of the carbon-H^{+} surface complexes is less than that for the carbon-Cd(II) complexes, then a rise in temperature

would reduce the tendency of carbon-H^+ formation and, as a result, decrease its competition with Cd^{+2} for the carbon sites. The effect would be greater, of course, at more acidic pH values since the H^+ concentration is greater. Hence, this may explain, at least qualitatively, why temperature changes have a more significant impact at lower pH. However, due to the lack of information as to the precise nature of the activated carbon surface functional groups and the thermodynamic properties of carbon surface complex formation, such a conclusion cannot be verified.

At higher pH values, H^+ competition becomes negligible, suggesting that another phenomenon is changing the adsorptive character of the system in this region. In the cyanide system, for instance, almost all of the cadmium is present in the form of $Cd(CN)_3^-$ and $Cd(CN)_4^{-2}$ complexes at pH 8.5 (see Fig. 4, page 46). Carbon adsorption of these species is unfavorable from an electrostatic viewpoint, since the surface is also negatively charged at pH 8.5. However, ΔH values are given for the Cd-CN complexes as follows: $\Delta H\text{-}Cd(CN)^+ = -7.4$, $\Delta H\text{-}Cd(CN)_2 = -7.7$, $\Delta H\text{-}Cd(CN)_3^- = -7.1$, and $\Delta H\text{-}Cd(CN)_4^{-2} = -7.0$ kcal/mole (35). The negative sign indicates that a rise in temperature will suppress Cd-CN complex formation, implying that a larger percentage of the total cadmium in solution at pH 8.5 will be in the Cd^{+2} form. These cations have a greater affinity for the carbon surface at pH 8.5 than do the negatively charged species, thus accounting for the increase in removal for increasing temperature.

It should be noted that temperature effects on adsorption equilibria usually are not regarded to be substantial (40). In addition, the temperature range encountered in cadmium wastewaters will undoubtedly be small relative to that employed in the context of this research.

Desorption (Single-Stage)

Regeneration of the exhausted carbon is essential if the activated carbon adsorption process is to be economically feasible in practice. In order to gain some insight into the reversibility of the adsorption reaction, as well as the possibilities for regeneration, desorption experiments were conducted with four activated carbons for the cadmium fluoborate solution.

Following a two hour adsorption period, the cadmium-laden carbon was separated from solution and immersed into another solution of distilled water and ionic medium at the same pH and temperature. Figures 28 and 29 show the amount of Cd(II) released back into solution by the carbon after two hours of reaction. The solid line is the adsorption density as a function of pH. The dashed line is a measure of the amount of Cd(II) still attached to the carbon, and thus retains units of μM/g. The "band" between these two lines represents the amount of cadmium desorbed. As presented here, the units are μM/g, but these values can easily be converted to total number of moles of Cd(II) desorbed by multiplying by two. The remaining solid line gives the percentage of the Cd(II) originally adsorbed which has now been desorbed, the values of which are read directly from the right-hand ordinate.

The obvious trend in the data is that the percentage desorbed increases with decreasing pH for all four of the carbons studied. Mathematically, this

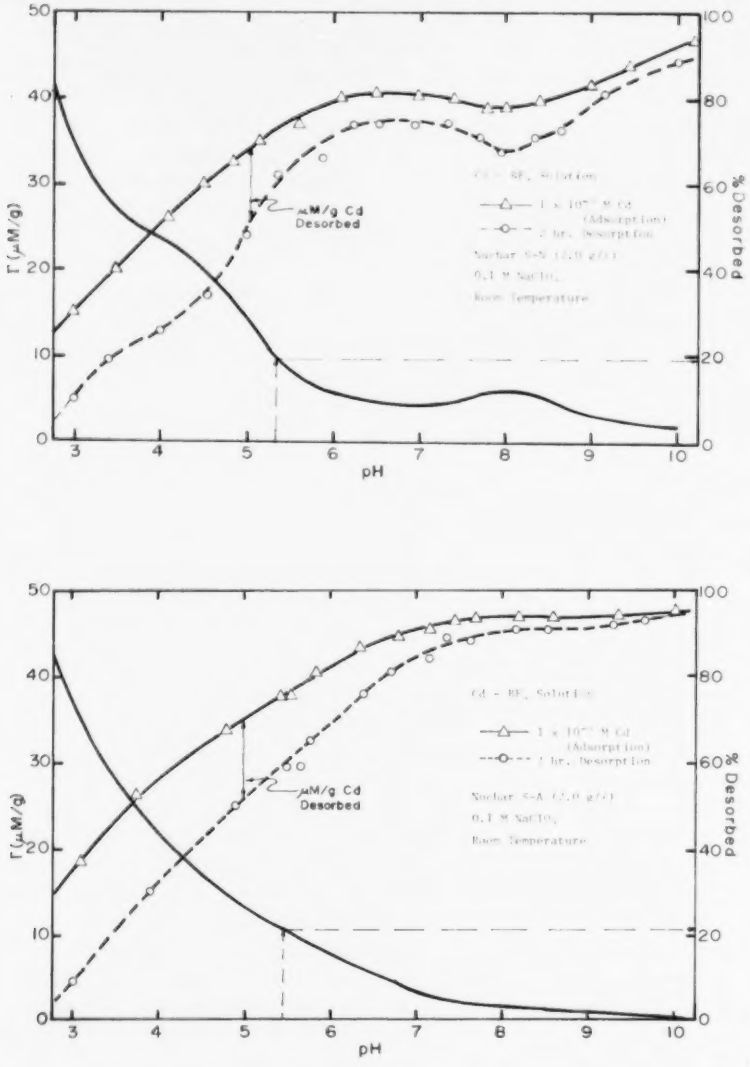


Figure 28. Extent of desorption of Cd(II) in Cd-BF_4 solution as affected by pH: (a) Nuchar SN (top); (b) Nuchar SA (bottom). Original adsorption data (Δ); desorption data at corresponding pH (o); percentage of adsorbed Cd(II) that became desorbed at the various pH (——). Total initial Cd(II) for adsorption = 10^{-4} M, carbon concentration for adsorption = 2 g/ℓ, 0.1 M $NaClO_4$.

is to be expected, assuming a constant desorption band, since adsorption of Cd(II) decreases with decreasing pH. However, for Nuchar SA and Nuchar SN, the desorption band actually widens with decreasing pH. The percent desorption curves are almost identical for these two carbons, with both attaining approximately 80 percent Cd(II) desorption at pH 3. For the granular carbons,

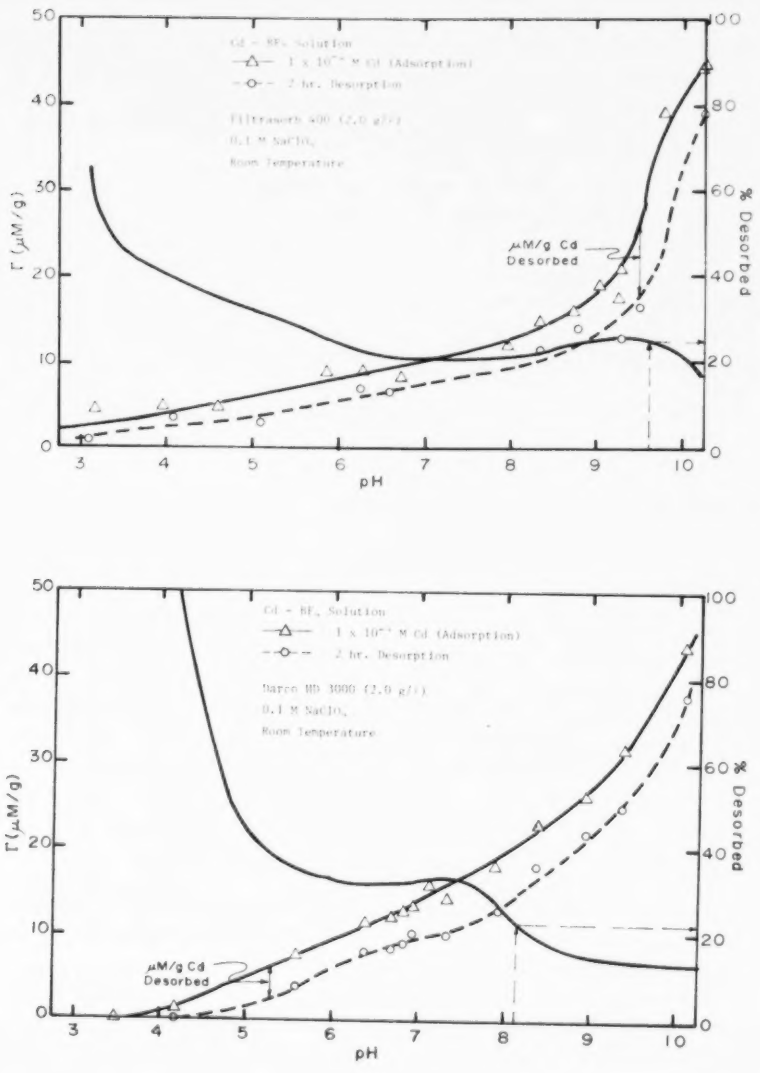


Figure 29. Extent of desorption of Cd(II) in Cd-CN solution as affected by pH. Symbols and conditions are same as Figure 28.

the band width is relatively constant for all pH values. However, percent desorption values at low pH for these carbons cannot be regarded as meaningful due to the very small extent of adsorption there.

It is difficult to explain the nature of the desorption band for the powdered carbons, particularly in light of the fact that specific adsorption is not considered to be readily reversible and yet is probably responsible for Cd(II) adsorption at low pH. On the other hand, electrostatic adsorption is certainly important at pH values greater than the pH_{zpc}, and is considered

to be readily reversible (49). This serves to point out the complex nature of activated carbons and the difficulty in characterizing their behavior in solution.

One clear indication from the desorption data for the powdered carbons is that regeneration may be accomplished by treating the carbon with strong acid, for example HNO_3 or $HClO_4$. The addition of small amounts of acid would strip the Cd(II) from the surface of the carbon, and hopefully retain the metal in a form that is concentrated enough for possible recovery.

The rate of desorption was found to be similar to that of adsorption, in the sense that the maximum level of Cd(II) desorbed was attained within the first ten minutes of contact of the carbon with the fresh solution.

Pretreatment of Activated Carbon with Carbon Disulfide

Several successful attempts have been made by other researchers to improve the removal capabilities of various adsorbents by employing sulfurizing treatments. Humenick and Schnoor (55) cited Yokota who showed that charcoal activated with dithizone sulfurizing agent would remove mercuric chloride in the presence of excess chloride. In another work, carbon disulfide (CS_2) containing 40 percent sulfur was successfully used to give good sulfur penetration of a cotton cord adsorbent for the treatment of mercury in stream and lake sediments (56). A more recent study by Humenick and Schnoor (55) indicated that carbon disulfide could react with activated carbon to form chelating groups such as xanthates, dithiocarboxylates, or dithiocarbamates. Their experimental results showed that presoaking activated carbon in CS_2 significantly increased mercury adsorption at both high and low pH values. They proposed a chemisorption mechanism, i.e., a chemical bond may have formed between the CS_2 molecule and the mercury ion.

These previous treatments all involved mercury adsorption. However mercury, like cadmium, is a member of the IIB periodic family, and as such the two possess some chemical similarities. Sulfur atoms have a high affinity for cadmium, as evidenced by the K_{sp} of cadmium sulfide ($K_{sp} = 10^{-27.2}$) (35). Thus, a process was employed using sodium methylate and liquid CS_2 which tried to attach a sulfide functional group to the activated carbon surface that would react more readily with Cd(II). This process was attempted with the granular carbon, Darco HD 3000, and the proposed mechanism is represented schematically in Fig. 30.

When sodium methylate (CH_3ONa) is reacted with the activated carbon, the sodium ion replaces the hydrogen ion associated with the O-H group on the carbon surface. Upon addition of CS_2, the oxygen "attachs" the carbon atom, forming a new functional group depicted as (3) in Fig. 30. When this carbon is added to a solution containing Cd(II), the Cd^{+2} ions will replace Na^{+} ions as shown in (4). This process assumes, of course, that the activated carbon possesses a strong alcohol or phenolic group on its surface. If not, the CS_2 will not attach and will simply be washed out of solution as a yellow-colored filtrate.

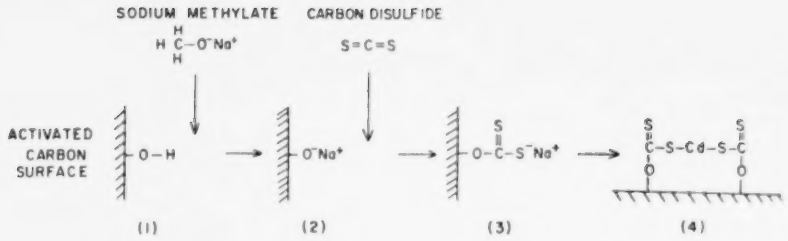


Figure 30. Proposed mechanism for Cd(II) removal as a result of pretreatment of Darco HD 3000 with liquid CS_2.

Initial tests using this pretreatment scheme showed improved Cd(II) removal. However, in subsequent trials, when the carbon was washed very thoroughly before drying and use, batch experiments yielded data indicating little or no increase in Cd(II) adsorption. Some of these results are shown in Fig. 31. The solid line depicts adsorption vs. pH for the untreated carbon, while the data points are for the pretreated carbon. The apparent success of the first trial was probably due to the entrainment of solution containing the sulfur group within the pores of the carbon, which upon more thorough washing was removed.

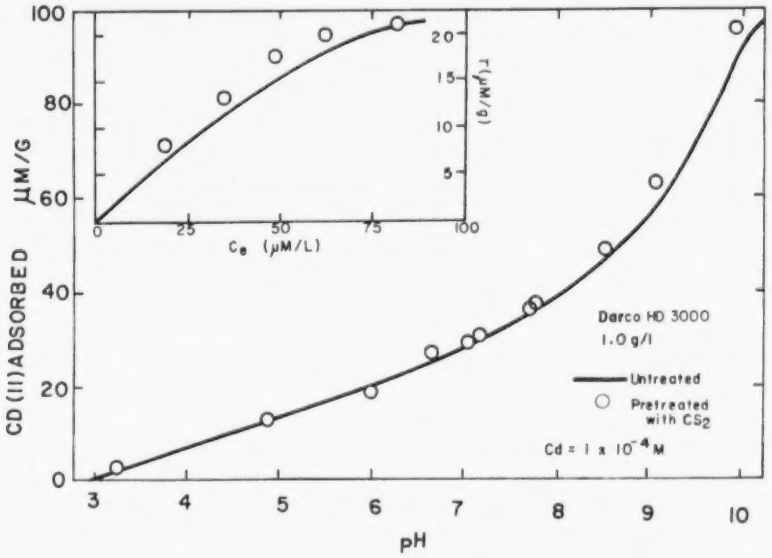


Figure 31. Comparison of Cd(II) adsorption using treated and untreated Darco HD 3000 activated carbon.

The results indicate that the O-H functional group is not prevalent on the surface of Darco HD 3000. Yet this group is one that is often suggested

as being present on activated carbons (21-24). Thus, further investigation of this process involving other brands of granular activated carbon is warranted.

SUMMARY

The results indicate that cadmium can be appreciably adsorbed from electroplating wastewaters using certain commercially available carbons, namely Nuchar SA and Nuchar SN.

The kinetics of the adsorption were very favorable for both the fluoborate and cyanide systems using these carbons. The maximum adsorption level was reached within the first 10 minutes of contact of the carbon with the wastewater. This rapid rate of removal was unaffected by variations in pH, ionic strength, carbon dose/[Cd(II)] ratio, temperature, and mixing rate. It also renders the carbon adsorption process more effective than chemical precipitation which is often a slower process.

The important parameters with respect to the extent of Cd(II) adsorption are carbon type, carbon dose/[Cd(II)] ratio, pH, wastewater composition, and ionic strength. Nuchar SA and Nuchar SN, powdered carbons, were shown to have a Cd(II) adsorption capacity far superior to that of the granular carbons tested, namely the Filtrasorb and the Darco brands. This is postulated as being due to the presence of certain functional groups on the surface of the powdered carbons which have a greater chemical affinity for Cd(II) species in solution.

For the same carbon dose, the adsorption density increases for increasing Cd(II) concentration in solution. The Cd(II) concentration range of interest for electroplating wastewaters is 5×10^{-5} M to 5×10^{-4} M, with a typical value being 1×10^{-4} M or 11.24 ppm. However, the percent of cadmium removed begins to decrease for higher initial concentrations of adsorbate, particularly in the acidic pH range. At pH values greater than 8, this effect is not as noticable due to precipitation effects in the fluoroborate bath, and cadmium cyanide complex formation in the cyanide system. For a given Cd(II) concentration, an increase in carbon dose yields a higher percentage of cadmium removal, but a lower adsorption density value.

The hydrogen ion concentration of the wastewater solution plays a critical role in the extent of Cd(II) adsorption. For both the fluoroborate and cyanide wastewaters, the adsorption density was found to approach its maximum level in the neutral pH range. This is another positive feature of the activated carbon process when compared to the more commonly used cadmium removal technique of precipitation, which requires pH adjustment to at least 10-11 for maximum removal. Nuchar SN is particularly effective in this regard, with little or no pH adjustment required after addition to solution.

Two different models were applied to the experimental results in order to attempt to describe the extent of Cd(II) adsorption and the pH effect. A modified Langmuir adsorption isotherm describes the equilibrium adsorption data very well for the fluoroborate and cyanide systems over the cadmium concentration range of interest. The modification involves integrating the effect of the hydrogen ion concentration, which acts as a competitive inhibitor to

Cd(II) adsorption in a pattern analagous to the inhibitory effect of certain substances to enzyme metabolism. The resulting Langmuir equation is:

$$\frac{1}{\Gamma} = \frac{1}{\Gamma_m} + \frac{K_m}{\Gamma_m}\left(1 + \frac{[H^+]}{K_i}\right)\frac{1}{C_e} \qquad (10)$$

where C_e is the equilibrium Cd(II) concentration, Γ is the adsorption density at C_e, Γ_m is a measure of adsorption capacity, and K_m and K_i are the rate constants for the carbon-Cd(II) and carbon-H^+ reactions respectively. The constants Γ_m, K_m, and K_i allow for meaningful comparisons to be made for different adsorption systems.

Cadmium adsorption from the fluoborate system is higher than from the cyanide wastewater. This is due mainly to the high molar ratio of CN:Cd(II) of 10:1, resulting in competition between the two ions for available carbon sites. This problem can be overcome by reducing the initial cyanide concentration in the wastewater, or by increasing the carbon dose.

Cadmium adsorption was seen to increase for decreasing ionic strength of solution. This is significant in light of the fact that the ionic strength used in experiments, 0.1 M as $NaClO_4$, is higher than that normally encountered in actual plating wastewaters.

SECTION 6

COLUMN MODE STUDIES

Based on the preliminary batch experiment results, a selection was made for the carbon to be used in a bench scale treatment set-up for a synthetic cadmium plating waste. A powdered type carbon was chosen. In order to contain the carbon particles (dia. 4-5 μm) in a continuous flow reactor without the formation of an undesirable headloss, the carbon particles were bound into porous beads (dia. 0.6 mm) using a suspension-polymerization technique. Experiments were run using a cadmium fluoborate synthetic plating wastewater composition in order to determine the equilibrium adsorption isotherms and the kinetic behavior of the carbon beads. A quantitative kinetic equation was formulated based upon bimolecular reaction considerations, along with theories related to the study of catalysis. Regeneration experiments were performed in order to determine possible reactivation of the surface following the adsorption cycle. Finally, continuous flow experiments were conducted in order to determine the behavior of the activated carbon beads in a bench scale set up.

EXPERIMENTAL

Activated Carbon Beads

The activated carbon beads were made based on a suspension-polymerization technique used by Light (57) and Weiss (58) for ion exchange resins. The technique involves a crosslinking reaction between two polymers in order to form a three dimentional matrix that entraps the carbon particles (4-5 microns) while maintaining a porous structure allowing for ion diffusion to occur within the carbon beads. The two polymers used were polyvinyl alcohol (PVA) and glutaraldehyde. The polymers were mixed in such a fashion so that the added glutaraldehyde concentration would react with 20 - mole -% of the hydroxyl groups of the PVA.

The procedure for the process is as follows. First 25 grams of the powdered carbon were added to 200 mℓ of distilled-deionized water and mixed with a mechanical stirrer. The pH of the slurry was adjusted to 1.65. The pH of the slurry required approximately 30 minutes to equilibrate. After equilibrium was reached the powdered carbon particles were filtered with a millipore membrane filtering apparatus (0.45 micron) and saved for a later step. The crosslinking reaction between the PVA and glutaraldehyde is acid catalized, thus requiring a specific pH in order to attain a satisfactory rate of reaction. In a separate 400 mℓ graduated beaker, 10.73 grams of PVA along with 1.07 grams of sodium chloride (NaCl) were added to 130 mℓ of water and heated to 85 ½C using a constant temperature bath (Thermomix 1460, Braun Corp.) in order for the PVA to totally dissolve. After the solution dissolved, the

pH was adjusted to 1.65. The filtered carbon particles were then added and mixed in order to form an uniform slurry. Before addition of the glutaraldehyde, a 4000 mℓ graduated beaker was filled with three liters of transformer oil and left to mix at a speed of 1600 rpm using a marine type stirrer (Non-Aerating Stirrer, Kraft Apparatus, Inc.). The stirrer was mounted off-center of the beaker to assure more turbulent mixing. The 25% - glutaraldehyde solution, a 5.7 mℓ volume, was added to the polymer-carbon slurry and mixed vigorously for one minute. The slurry was then immediately transferred into the turbulent transformer oil where rapid mixing formed tiny carbon beads, suitable for continuous flow reactors. The stirring continued for two hours at 1600 rpm and for two more hours at a slower speed, in order for the cross-linking reaction to complete. The oil was then decanted from the beaker and the beads were washed in order to remove the oil from the pores. Six cycles were used to wash the beads, three using acetone, 45 minutes apiece, and three cycles with distilled-deionized water to remove the acetone, 45 minutes apiece. The beads were then cured for 90 minutes under a vacuum at 105 °C and then air dried overnight. The carbon beads were then sorted into appropriate size fractions using conventional sieves. Further information on the basis of the suspension - polymerization technique can be found in the references. The carbon beads were sieved into three fractions; namely, 0.250 mm - 0.425 mm, 0.425 mm - 0.833 mm, and 0.833 mm - 1.000 mm.

TABLE 12. Composition of the Carbon - PVA Beads

PVA(g)	Carbon(g)	Glutaraldehyde (25%)	NaCl(g)	%-wgt. PVA
10.73	25.00	5.67 mℓ	1.07	30

Polyvinyl Alcohol

The polymer was supplied courtesy of the DuPont Company. The polyvinyl alcohol, 'ELVANOL HV' was used for the polymer crosslinking reaction in conjunction with a 20%-glutaraldehyde solution in order to form carbon beads of a size suitable for a continuous flow reactor. Properties of 'ELVANOL HV' are given in Table 13.

Batch Adsorption Experiments

The procedure for the batch adsorption experiments is as follows. First, appropriate quantities of the ionic strength solution ($NaClO_4$) to give an I = 0.01 M, distilled-deionized water and cadmium solution were added to a 125 mℓ polypropylene bottle. The carbon, either added from a 10 or 25 gram/liter slurry if used in the powdered form, or weighed if used in the granular or bead form, was then added. pH adjustment was then made with 0.1 M and 1.0 M perchloric acid and sodium hydroxide using a Corning Model 12 Research pH

Meter equipped with a Beckman-Combination pH electrode. The pH range for the batch samples varied between a pH of 3 up to a pH of 10. After pH adjustment, the samples were taken in a reciprocating shaker for 12 hours at room temperature. After shaking the final equilibrium pH was recorded. The carbon was removed from solution by filtration using a membrane filtering apparatus (0.45 μm). Metal analysis of the supernatant was performed by means of flame atomic absorption spectroscopy using a Jarrel-Ash Model 810 Atomic Absorption Spectrophotometer at wave length 2288 A. Calibration standards of similar ionic strength were prepared in order to avoid matrix interference effects.

TABLE 13. Properties of 'ELVANOL HV'

Viscosity, 4% water solution mPa s(cP)*	55 - 65
Solution pH	5 - 7
Percent hydrolysis†	99.0 - 99.8
Volatiles, T by wt. max.¶	4%
Ash, % by wt. max.	1%

*Determined at 20 °C by Hoeppler Falling ball method
†Mole percent hydrolysis of acetate groups, dry basis
¶Dry basis; calculated as % Na_2O

Kinetic Experiments

Batch kinetic experiments were conducted as follows. First, appropriate quantities of the ionic strength solution, distilled-deionized water, and cadmium solution were added to produce a 500 mℓ volume of desired solution. This solution was placed in a 600 mℓ pyrex graduated beaker with a pH adjustment performed. A marine type stirrer was used to provide continuous mixing. The carbon beads were added to the stirring solution and the pH was maintained at a constant value throughout the experiment. Magnetic stirring bars were not used since abrasion of the beads would occur and as a result, the kinetic data would be invalid for the given carbon bead size. At the end of a prescribed time interval, 10 mℓ of the solution were pipetted and filtered using a millipore filter (0.45 microns). The concentration of the residual Cd(II) in the supernatant was determined.

Continuous Flow Experiments

All continuous flow experiments were conducted using a column reactor. The column consisted of a plexiglass tube with an inside diameter of 2.54 cm (1 inch) and a length of 33 cm (13 inches). The amount of carbon was determined by mass and placed in the column with glass wool to insure even distribution of flow at both ends of the column. Synthetic wastewater, 10^{-4} M $Cd(BF_4)_2$, with the pH adjusted to 7 was delivered to the column using a varying speed peristatic pump (Cole-Palmer Masterflex) at a constant flow rate of 8.2 mℓ/min/cm^2 (2 gallons/min/ft^2). Samples were collected into 75 mℓ pyrex test tubes with a fraction collector (Eldex Universal). The column operation is illustrated in Fig. 32. The concentration of the residual Cd(II) in the supernatant was determined.

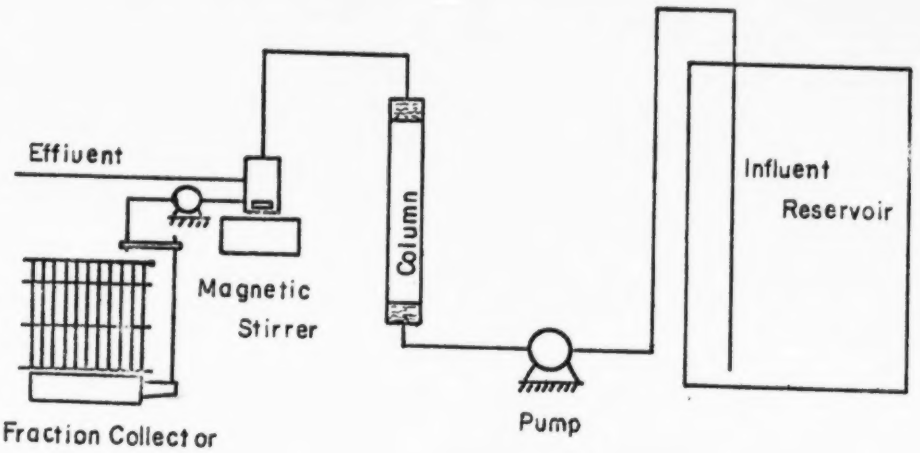


Figure 32. Experimental set-up for column runs (not to scale).

Regeneration of Activated Carbon

Batch adsorption experiments were first conducted to achieve specific adsorption densities (or surface coverage or surface loading) on the surface of the carbon beads. The cadmium-laden carbon beads were then placed in 125 mℓ polypropylene bottles with various volumes of acid to determine the minimum volume needed to desorb the cadmium from the surface. Three acids were examined: perchloric acid ($HClO_4$), hydrochloric acid (HCl) and sulfuric acid (H_2SO_4). The samples were agitated for 24 hours at room temperature then subjected to filtration as described above for the analysis of residual Cd(II) in the supernatant.

RESULTS AND DISCUSSION

Following the preliminary screening, the selected carbon, Nuchar SA was bound into beads and comparative experiments were conducted for the adsorptive behavior of the powdered and aggregated forms. Fig. 33 illustrates the adsorption behavior of the two carbons as a function of pH. Above pH values of 8.5, two mechanisms are responsible for removal of Cd(II), adsorption and precipitation. Removals for both carbon forms are similar for this pH range.

TABLE 14. Specific Surface Area*-Nuchar SA

Type	Surface Area (m^2/g)
Powdered	760
Beads	730

*Determined by the Nitrogen BET Method

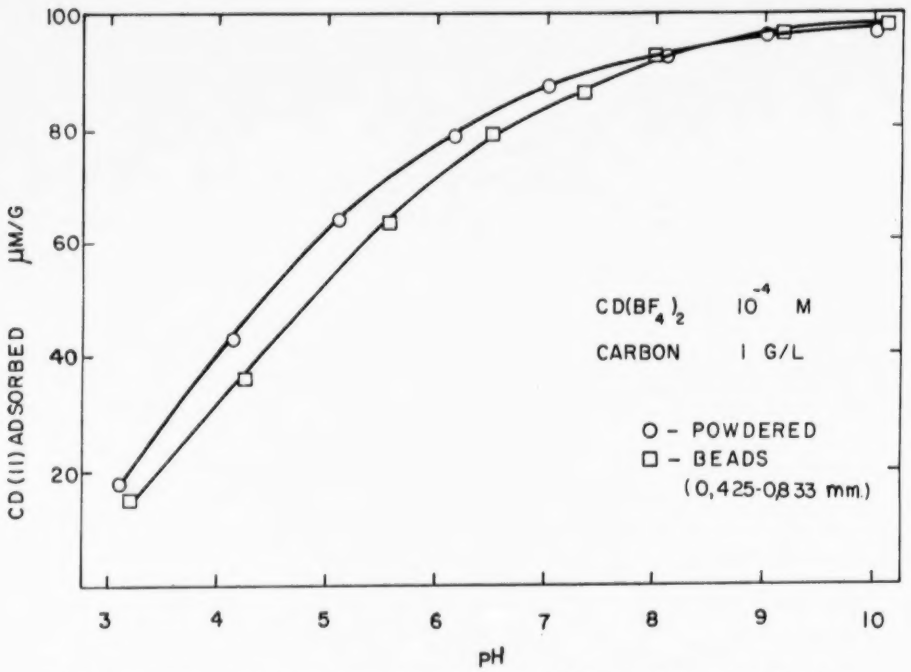


Figure 33. Adsorption density as affected by pH of the activated carbon beads (Nuchar SA).

Equilibrium Adsorption Isotherms

Adsorption isotherms are useful in describing adsorption data with regard to design considerations. Isotherms show the relationship between the bulk activity of adsorbate and amount adsorbed at constant temperature. This is important when considering reaction configurations for treatment schemes. Efficient use of any adsorbent is dependent on the optimal use of the available adsorption density. Fig. 34 shows the adsorption isotherms for Nuchar SA. A typical plating waste contains 10^{-4} M Cd(II) or 100 µMoles/liter Cd(II). The equilibrium adsorption density, Γ_e, for this equilibrium cadmium concentration, C_e, is 270 µMoles/gram. This implies that one gram of carbon is capable of treating 2.7 liters of waste water provided all the Γ is utilized. The amount of surface utilization for treatment schemes is dependent on reactor configurations that take advantage of the Cd(II) concentration gradiant existing in the reactor.

Adsorption Kinetics

The rate at which dissolved substances are removed from dilute aqueous solutions by solid adsorbents are controlled by three consecutive steps: film diffusion, pore diffusion and adsorption (47).

Film diffusion deals with the transport of ions from the bulk solution to the surface of the solid adsorbent. A boundary layer or film is believed to exist at the surface of the adsorbent that hinders transfer to the solid surface. Film diffusion rarely controls rate of adsorption when a complete

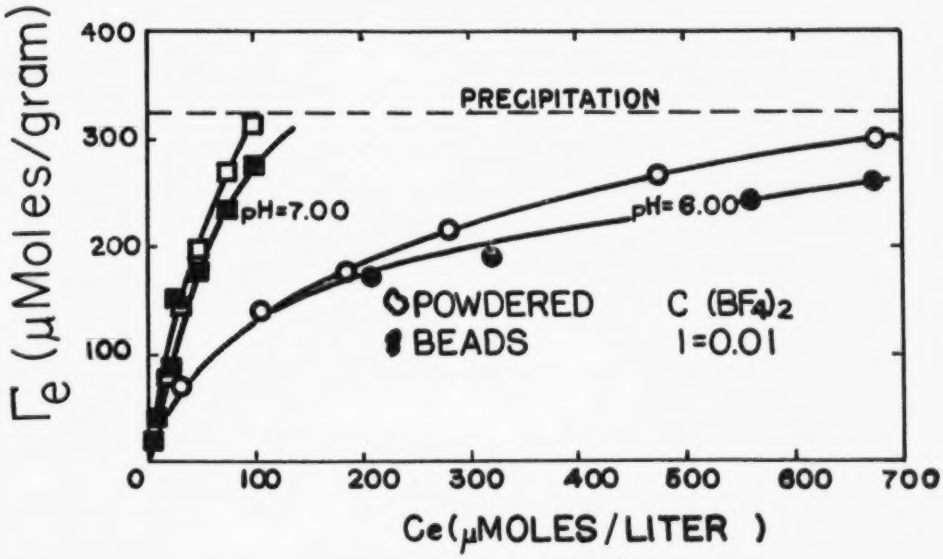


Figure 34. Adsorption isotherm of the activated carbon beads (Nuchar SA).

mix criterionis satisfied. Pore diffusion, the second step of the process, deals with the diffusion of ions within the pores of the absorbent. This step is usually the rate limiting step for adsorption using granular media in complete mix reactors. Adsorption, the final step of the process, is probably not a rate limiting step based on the powdered carbon adsorption data presented. Also, Weber (47) indicated adsorption of chemical compounds that lower interfacial tension are adsorbed at a very quick rate. This also suggests that adsorption is probably not a rate determining step.

Adsorption kinetic information of carbon adsorption of cadmium is prerequisite to reactor design. A comparison of the kinetics of the powdered and bead form of Nuchar SA, shown in Figure 35, shows a distinct difference in rates of adsorption. Results of the powdered data indicate that adsorption is very rapid with equilibrium obtained in less than thirty minutes. Mass-transfer plays an insignificant role for powdered carbons due to their small size (4-5 microns) and the very short diffusion paths the Cd(II) ions have to travel prior to adsorption. The aggregated form of the carbon is mass-transfer limited by intraparticle diffusion. The porous bead structure requires the Cd(II) ions to diffuse into the solid prior to adsorption, explaining the slower rate of removal compared to the powdered form.

The quantitative modeling of reaction kinetics of carbon adsorption is based upon two major considerations: (1) a bimolecular-type second order mechanism where the rate of adsorption of aqueous Cd(II) is directly proportional to the cadmium concentration and carbon in solution, and (2) the kinetics of heterogeneous catalytic reactions. Adsorption of cadmium onto activated carbon is similar in respect to catalysis in that similar steps

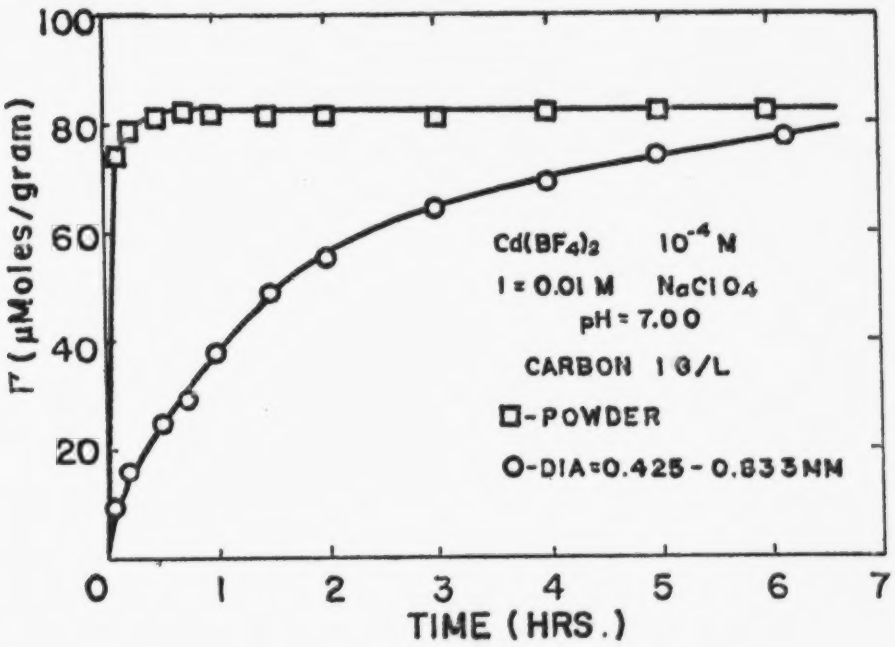


Figure 35. Comparison of adsorption kinetics between powdered and beaded carbon.

common to both processes occur. In catalysis, the reactions involve seven steps and are illustrated in Fig. 36.

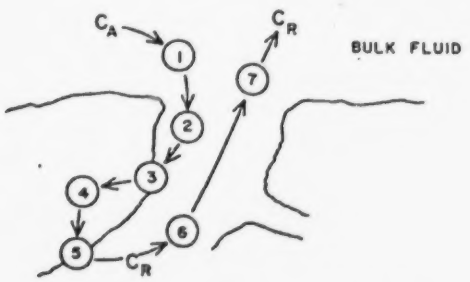


Figure 36. Steps involved in reactions on a solid catalyst.

The seven steps are:

1. Transport of reactants A,B... from the main stream to the catalyst pellet surface.
2. Transport of reactants in the catalyst pores.
3. Adsorption of reactants on the catalytic site.

4. Surface chemical reaction between adsorbed atoms or molecules.
5. Desorption of products R, S...
6. Transport of the products in the catalyst pores back to the particle surface.
7. Transport of products from the particle surface back to the main fluid stream.

Removal of cadmium involves the first three steps, terminating at the adsorption of reactants on the catalytic site. In terms of catalysis the solid surface is deactivated due to irreversible adsorption of some impurity in the feed stream, which is termed poisoning. This seems to parallel carbon adsorption of cadmium in terms of the probable events occurring in the solid, with cadmium as the poison in solution.

Wheeler (59) analyzed the kinetics of uniform poisoning in an idealized pore, and the results were generalized to catalyst particles. Fundamental to his development is the assumption that the catalytic site that has adsorbed poison on it is completely inactive. If Γ is the concentration of sites covered with poison, the fraction of sites remaining active, called the deactivation or activity function, is

$$\Phi = \frac{\Gamma_e - \Gamma}{\Gamma_e} \tag{11}$$

where Γ = the concentration of sites (carbon) covered with the poison (adsorbate)

Γ_e = the equilibrium concentration of sites covered with the poison dependent on the solution adsorbate concentration.

The following equation was proposed for the kinetic behavior for carbon adsorption of cadmium:

$$\frac{d[Cd(II)]ads}{dt} = k[Cd(II)][C]\{1 - \Gamma/\Gamma_e\} \quad ; \tag{12}$$

where $[Cd(II)]_{ads}$ = amount of Cd(II) adsorbed on the surface, (M/ℓ)

$[Cd(II)]$ = concentration of Cd(II) in solution, (M/ℓ)

$[C]$ = carbon concentration, (gm/ℓ)

Γ = adsorption density at time t (min.), (M/gm)

Γ_e = equilibrium adsorption density, function of $[Cd(II)]$, (M/gm)

k = rate constant dependent on the porosity and size of the carbon beads (ℓ/gm-min)

The pH-dependence of the kinetic equation is incorporated into the Γ term of the equation.

In order to determine the constant, k, the slope of the kinetic data, vs. time was plotted against the right hand side without the rate constant, k, of the equation. The resulting slope of the plot should equal k. Both coordinates were normalized in order to fit the data for various conditions

on one plot. Therefore the constant plotted, k_{plot}, is related to k by:

$$k_{plot} = k \frac{d[Cd(II)]_o/dt_o}{[Cd(II)][C]\{1 - \Gamma/\Gamma_c\}_o} \qquad (13)$$

The bracketed term of equation (13) was approximately equal to unity based on the Γ vs. time data; therefore, the plotted constant, k_{plot}, is approximately equal to the actual rate constant, k. Results of the actual data, the plots of the rate constant determination and the calculated (predictive) kinetics of adsorption are given in Fig. 37. Parameters, such as pH, initial Cd(II) and carbon concentration, and bead size were varied in order to determine the rate constant, k.

The fit between the calculated (lines) and experimental (data points) kinetics of Fig. 38 agree fairly well; however, looking at the graphs for the rate constant, k, one could argue against a linear fit of the data. The plots do not take into account the time factor involved regarding the data. Upon closer examination, it can be seen that the points deviating from the linear portion represent, time-wise, only the first hour or less of the kinetics. The remaining points represent the remaining fraction of the reactions and seem to fit a linear curve, denoting the rate constant, k.

The deviation of the kinetic equation to experimental data can be explained by several factors. The pore-size distribution is an important rate-controlling factor, and if not uniform, a variable rate constant will be observed. A non-uniform distribution of the carbon beads might explain the deviation of the data. Also, the porosity of the carbon beads can affect the kinetics if not uniform throughout the particles.

The overriding kinetic factor for most applications of granular activated carbons is pore diffusion (47). The data supports this view in that the rate constant was independent of pH, [Cd(II)], and [C] but dependent on the diameter of the carbon beads.

The calculated kinetic curves were obtained using a finite-difference method in conjunction with the computer. The algorithm is shown in Fig. 39 (60).

Surface Reactivation

The reactivation and reuse of a solid adsorbent after exhausting its usable adsorption capacity is desirable for practical applications. The adsorptive behavior of cadmium onto activated carbon follows a trend of decreasing adsorption with decreasing pH as illustrated in Fig. 33. The feasibility of desorbing Cd(II) from the carbon surface using strong acids while obtaining a favorable concentration of Cd(II) compared to the original wastewater was therefore investigated. Acid regeneration has also been suggested by previous workers dealing with carbon adsorption of chromium (VI) (61). Fig. 40 illustrates the results of the acid treatment on various surface loadings of Cd(II). The reductions in volume between the waste stream and the regenerate stream are shown in Table 15.

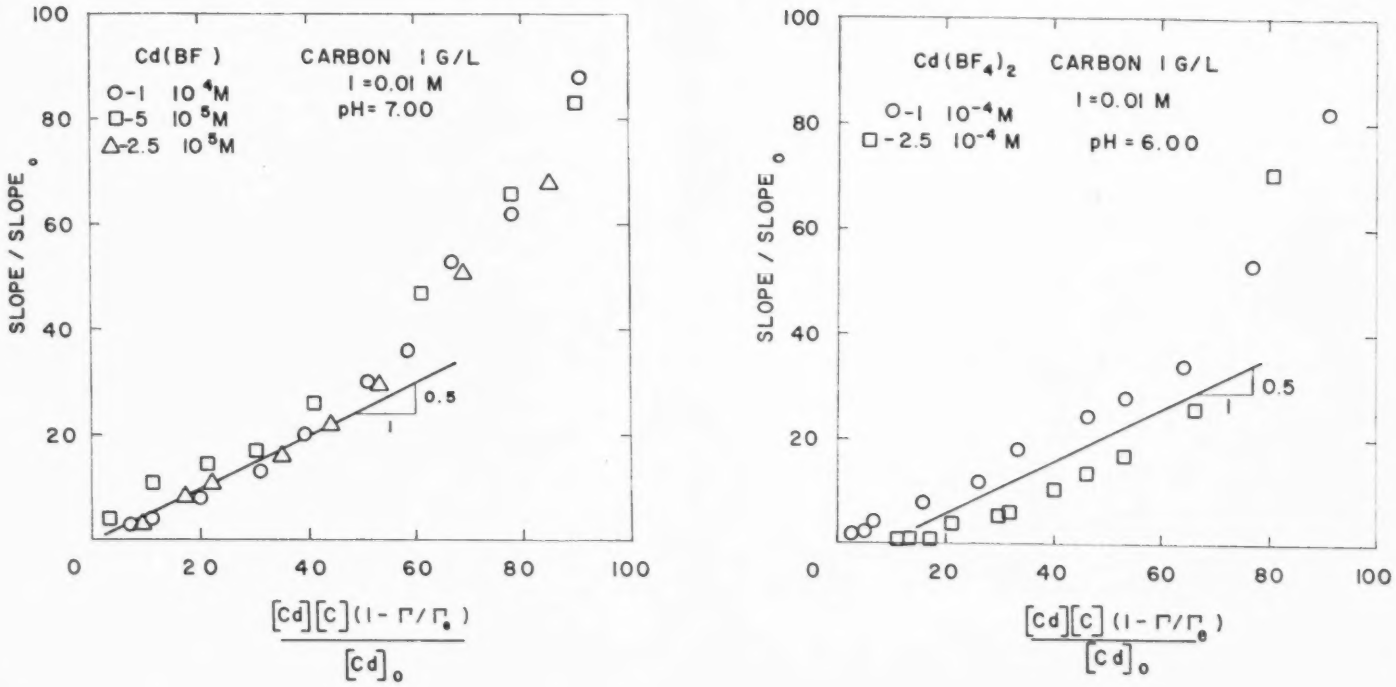


Figure 37. Plot for kinetic rate constant determination.
(a.) Based on Cd(II) concentrations at pH 7
(b.) Based on Cd(II) concentrations at pH 6

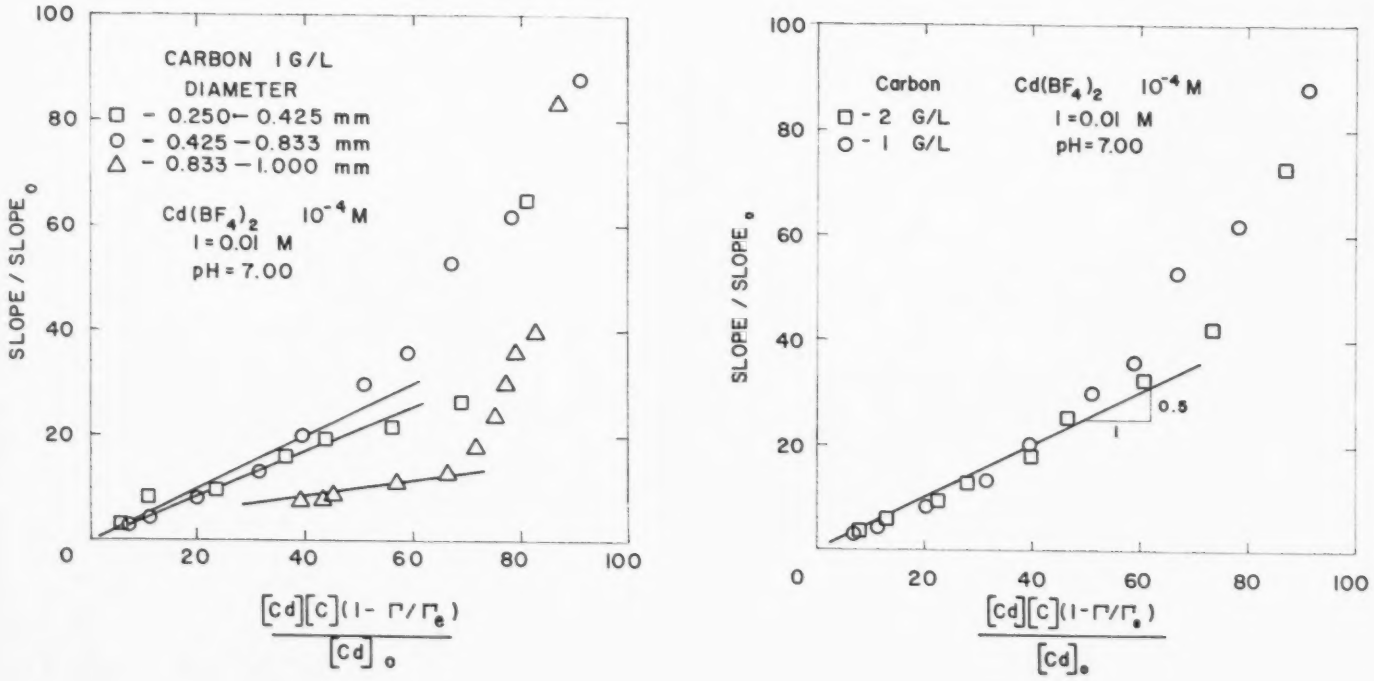


Figure 37. Plot for kinetic rate constant determination.

(c.) Based on particle size
(d.) Based on carbon dose

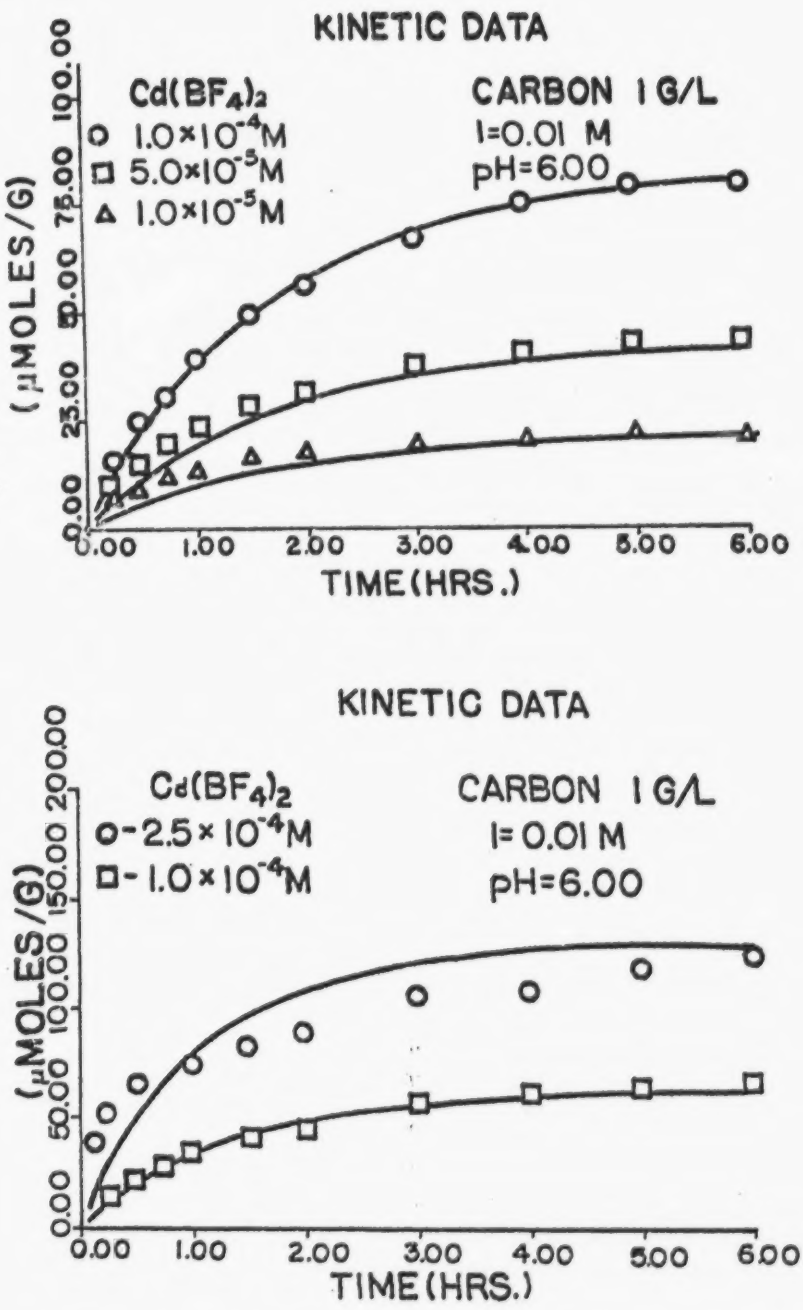


Figure 38. Kinetics of Cd(II) adsorption by activated carbon beads.

(a.) At Cd(II) concentrations from 1.0×10^{-5} M to 1.0×10^{-4} M (top).
(b.) At Cd(II) concentrations of 1.0×10^{-4} M and 2.5×10^{-4} M (bottom).

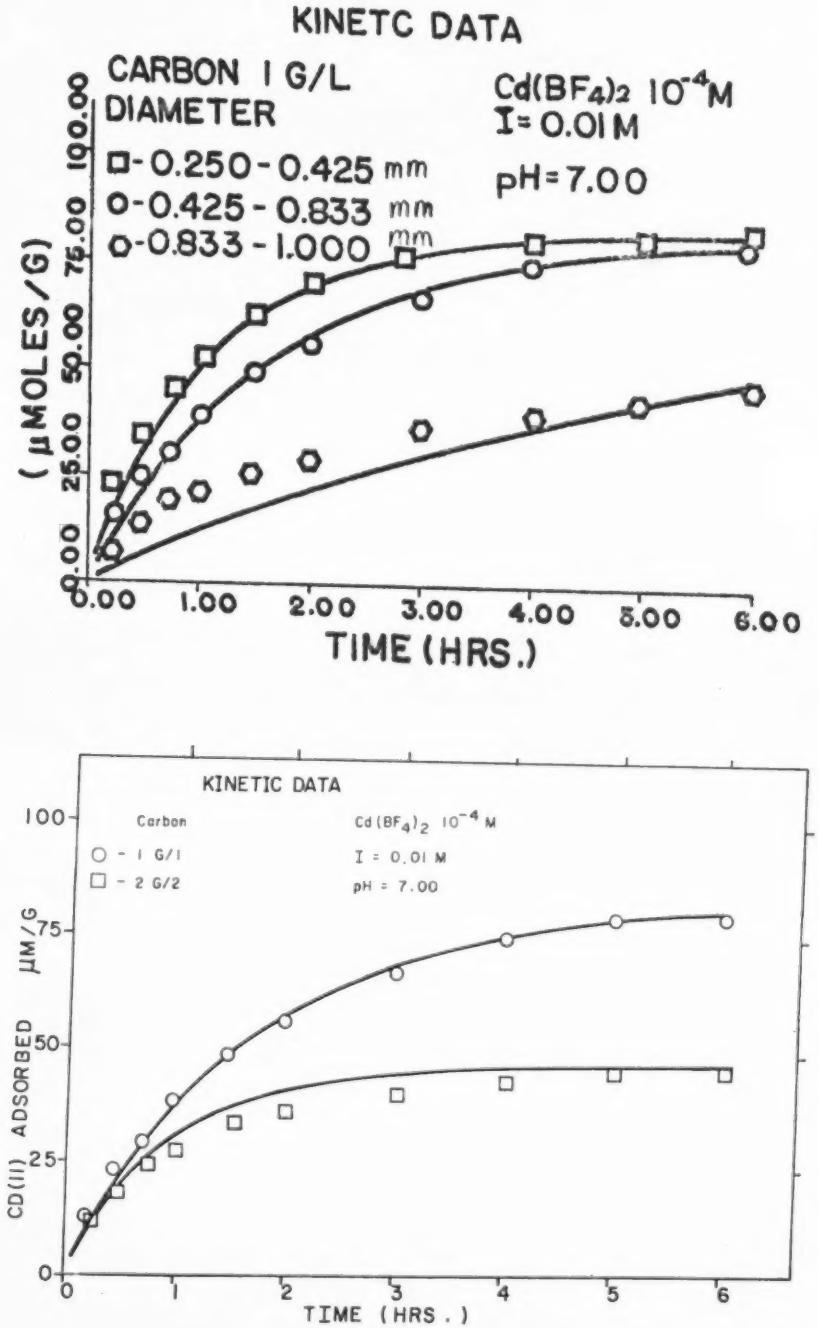


Figure 38. Kinetics of Cd(II) adsorption by activated carbon beads.

(c.) Effect of particle size (top).
(d.) Effect of carbon dose (bottom).

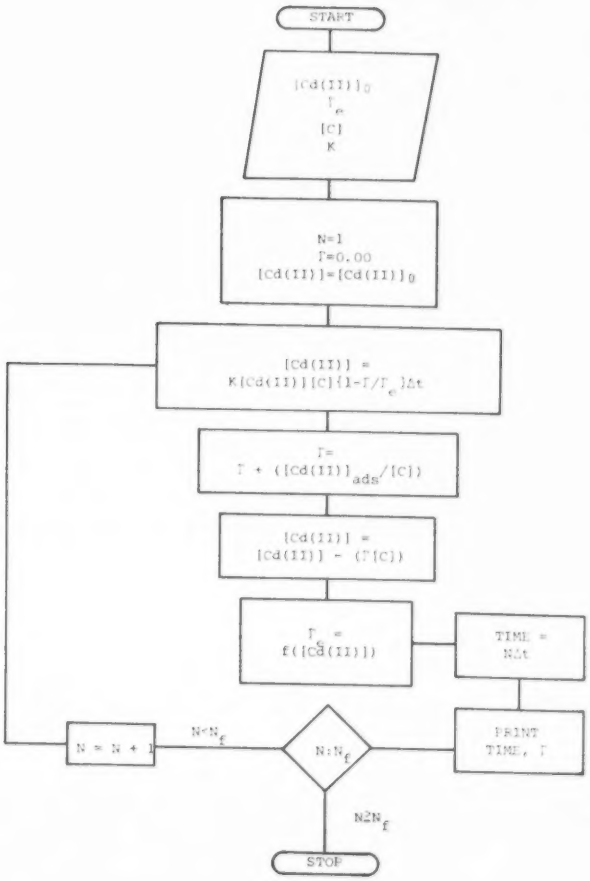
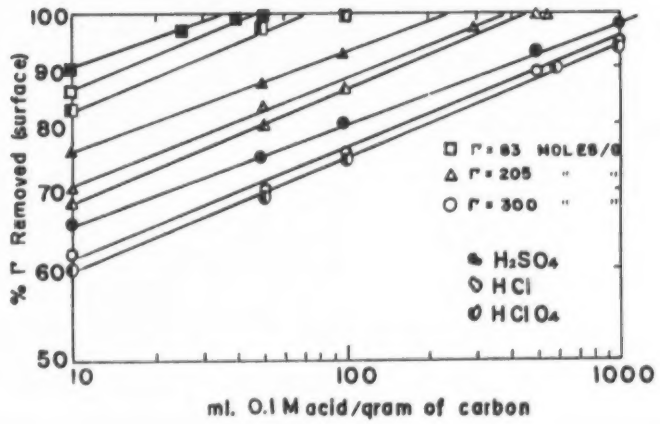


Figure 39. Algorithm for calculated kinetic curves (60).

TABLE 15. Comparison of Volume Reductions Using Various Acids Between the Waste Stream and Regenerate Stream at Γ 270 μMoles/gram,

Acid	(M)	Influent [Cd(II)]	Regenerate [Cd(II)]	Volume Reduction
HCl	0.1	10^{-4} M	2.57×10^{-4}	2.57
$HClO_4$	0.1	10^{-4} M	2.45×10^{-4}	2.45
H_2SO_4	0.1	10^{-4} M	2.7×10^{-4}	4.7
H_2SO_4	1.0	10^{-4} M	2.7×10^{-4}	27



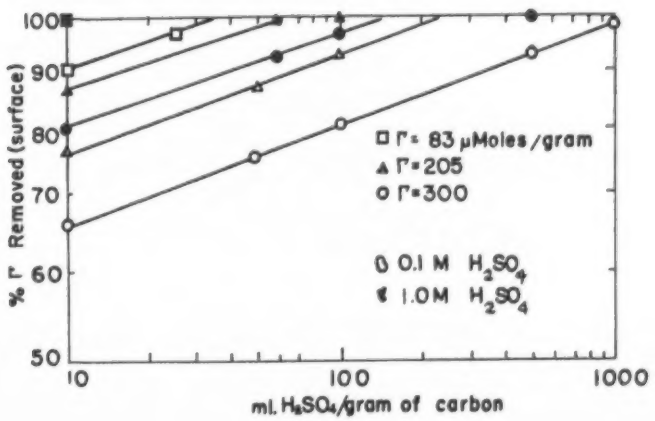


Figure 40. Regeneration of used carbon beads.

(a.) Different strong acids.
(b.) Different surface exhaustion.

This table indicates that 2700 mℓ of a 10^{-4} $Cd(BF_4)_2$ waste can be reduced to a 100 mℓ (1 M) H_2SO_4 solution per gram of activated carbon resulting in a volume reduction of waste of approximately 96%. This is a sizable reduction in the wastewater volume.

The results in Figure 41 give the kinetics of acid regeneration using 1 M H_2SO_4. The rate of regeneration depends on the extent of surface coverage. At a surface coverage level of 300 μmoles/gm (total coverage) total desorption took place in two hours. The regeneration time was 1.5 hours and 1 hour when the carbon surface was loaded with Cd(II) at 67% and 27%, respectively, of its capacity. The results indicate that the carbon can be used until the adsorption capacity is totally exhausted before being regenerated. The gain in regeneration at low surface loading (coverage) is marginal.

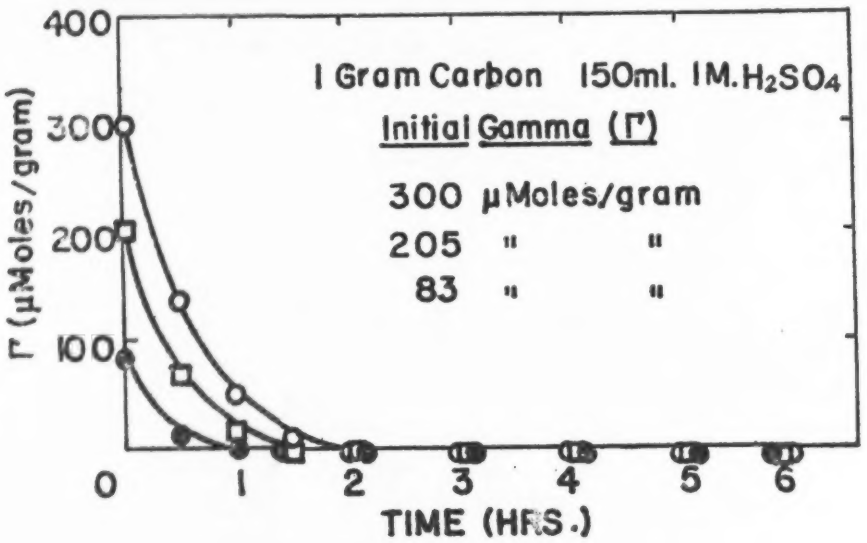


Figure 41. Kinetics of acid regeneration of used carbon beads.

Thermal regeneration was also considered for the desorption of Cd(II) from the carbon surface. However, for the temperature range, 25 °C - 90 °C, no appreciable desorption behavior was observed. Figure 42 illustrates the effect of temperature on desorption. The percent desorption at 25 °C tends to agree with the adsorption isotherm data indicating that the majority of adsorption is reversible.

Continuous Flow Experiments

A column reactor was used for all continuous-flow experiments. The results shown in Fig. 43 give the effluent concentration of Cd(II) from the column, run at a flow rate of 43 mℓ/min. (or 2 gal/min/ft^2). All values of effluent concentration prior to breakthrough (10^{-6} M Cd(II)) were actually

less than that reported, but recorded as such due to the limited sensitivity of the analytical procedure. A 99% removal of the influent concentration of Cd(II) was used for breakthrough. At the exhaustion point, the activated carbon was removed from the column and regenerated using 4.20 liters of 1.0 M H_2SO_4 for six hours. The carbon was then removed from the acid solution and placed in distilled water in order to adjust the pH of the carbon and water to a pH of 7.00 using NaOH. This process takes approximately 12 hours. The procedure was repeated between consecutive column runs.

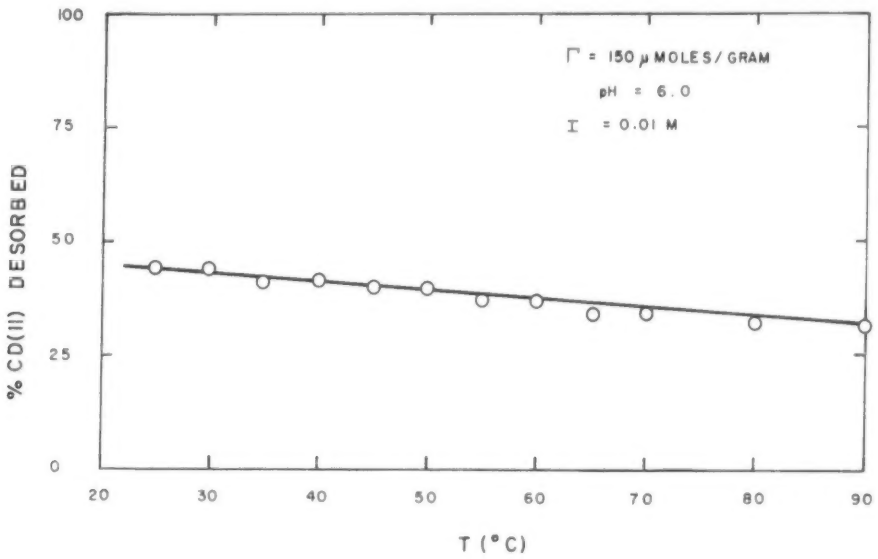


Figure 42. Thermal regeneration of Nuchar SA beads.

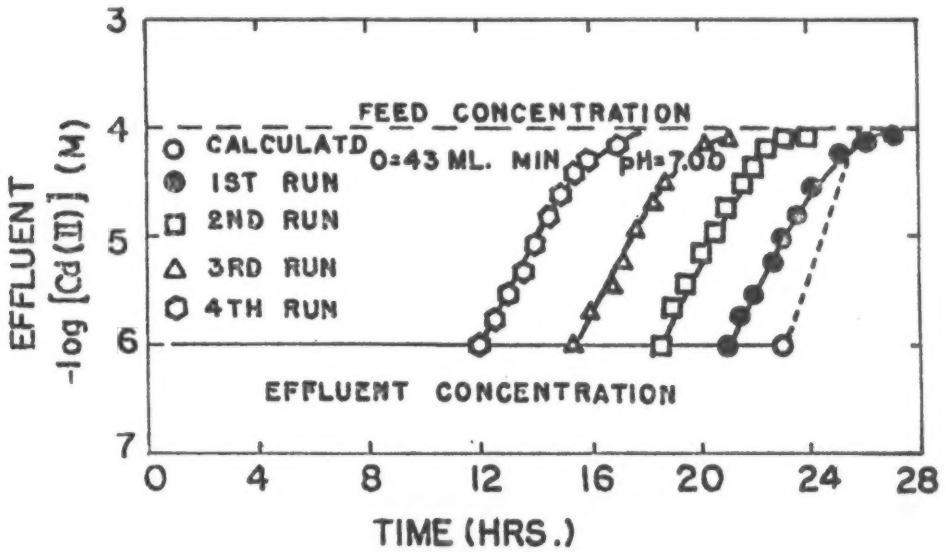


Figure 43. Results of column runs.

Table 16, along with Figure 44, shows the values of wastewater treated and the degree of surface utilization occurring prior to breakthrough. The results indicate that the breakthrough volume and surface utilization decreased after each successive run. A 20% reduction of volume was realized between each run. The loss of surface utilization capacity observed, due to acid regeneration has also been reported by Wu et al. (61). However, the reuse of the regenerated carbon is appealing even at a reduced efficiency. A total of 173 liters of wastewater (10^{-4} M Cd(II)) was treated for the total of four runs.

TABLE 16. Operational Results of Packed Column

Run	Liters Treated V_b*	Surface Utilization Γ/Γ_e (%)
1	59 (59[b])	64 (70[b])
2	48	57
3	40	48
4	31	37

[a]Column Diameter - 2.54 cm; Bed Depth - 21.5 cm; Carbon Bed - 40 gm total (28 gm carbon); Particle Size = 0.425 mm ∿ 0.833 mm (0.629 mm mean); Porosity = 40% (72% including pores).

[b]Calculated values from computer model.

The calculated value for breakthrough was based upon an approximation using a series of backmix reactors to simulate a virgin carbon bed (46). The efficiency of a column (plug flow) reactor is due to the existing Cd(II) concentration gradient. This configuration allows for optimal use of the available carbon surface for adsorption. However, the rate at which mass transfer occurs in the carbon bed is the controlling factor that determines the overall performance of the column reactor. This explains why the surface utilization was not 100% for the reactor. The agreement between the calculated volume and the first run is reasonable. Deviations between the two may be due to different mass transport phenomena. Weber has suggested that pore diffusion is often the rate limiting step for continuous systems, such as column reactors. However, the results between the calculated and first run are reasonable. The computer program for the column reactor can be found in the appendix.

SUMMARY

Factors affecting the adsorption of cadmium onto activated carbon are both intrinsic to the carbon surface and solution. The electrostatic nature of the carbon surface, quantified by electrokinetic methods, shows that the surface charge plays an important role in the affinity of the carbon for the Cd^{+2} .(aq) ions. Results have indicated that carbons with a low pH_{zpc} demonstrated the greatest affinity for cadmium species. Favorable electrostatic attraction encourages cadmium adsorption.

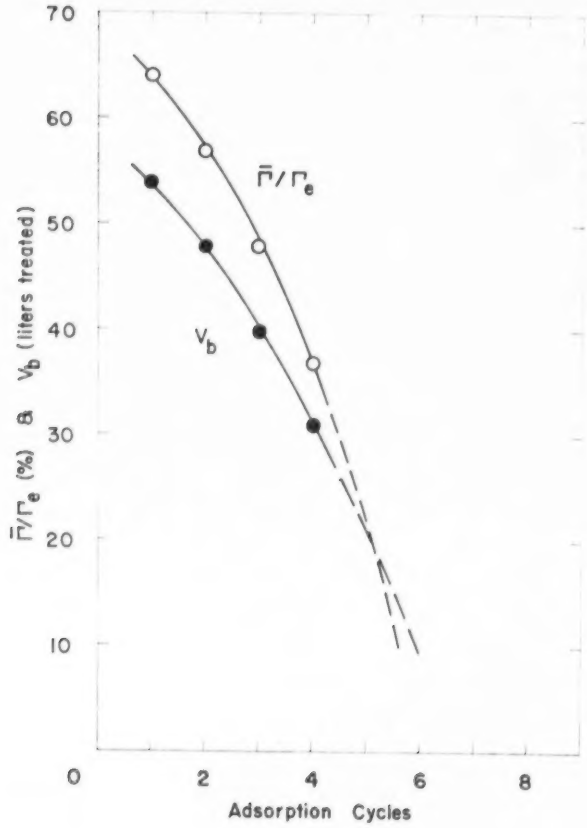


Figure 44. Column performance using regenerated carbon in consecutive adsorption cycles.

The solution pH also effects cadmium adsorption due to the pH-dependent surface charge of activated carbon. The cadmium species, $Cd^{+2}.(aq)$ is predominant over all others in the acidic and neutral pH range and is favorably adsorbed when the solution pH dictates a negatively charged surface.

The use of powdered activated carbon in continuous flow reactors requires the aggregation of the particles in beads suitable for a column reactor. This was accomplished by a suspension-polymerization technique. Results of the column runs, using a 10^{-4} M $Cd(BF_4)_2$ waste, with the pH of the waste and carbon beads adjusted to 7, indicate that roughly 50% of the surface capacity for cadmium adsorption was utilized for each of the four consecutive runs. Reactivation of the surface by strong acid was performed between runs. For 40 grams of carbon beads, the column reactor was able to treat 173 liters of wastewater prior to breakthrough at an effluent Cd(II) concentration of 10^{-6} M.

SECTION 7

SYSTEM DESIGN

Based upon the results presented above, two activated carbon adsorption treatment schemes are proposed.

TREATMENT OF THE Cd-BF_4 TYPE WASTEWATER

The solution chemical behavior of the $Cd(BF_4)_2$-containing waste solution is identical to that of the $Cd(ClO_4)_2$ solution (Fig. 5). The cadmium ions do not form complexes or ion pair with the anions, i.e., BF_4^- and molecule NH_3 to any significant extent and that Cd^{2+} ion is the predominant species over a wide pH range, e.g. 3 $\sim$ 9. The following treatment schemes are applicable to any wastewater than contains Cd^{2+} ion as the major species.

Completely Mixed Flow Reactor (CMFR)

Since powdered activated carbons such as Nuchar SA and Nuchar SN are superior to other brands of activated carbon in removing Cd(II) ions, it is therefore suggested that these types (acidic with low pH_{zpc}) of activated carbon be considered only. In the CMFR mode of operation (Figure 45), the powdered activated carbon is dispersed in the adsorption tank where the pH of the system is adjusted with lime or caustic to a neutral value for maximum adsorptive removal without precipitation. The formation of $Cd(OH)_2(s)$ precipitate may hinder solid-liquid separation operations that are to follow later. The Cd(II)-laden activated carbon particles are separated for regeneration and reuse. This is accomplished first by clarification, and thickening followed by acid (H_2SO_4) treatment and rinsing with water. Centrifugation can be used to separate the acid-regenerated carbon for reuse. The regenerant can concentrate Cd(II) approximately 27 times; which can be readily reprocessed for cadmium recovery.

While it is technically possible to treat cadmium plating wastewater by the CMFR mode, the process is limited by the availability of construction space and the efficiency of carbon separation; namely, sedimentation and centrifugation. Preliminary results from sedimentation experiments, without chemical conditioning, show that it is possible to separate the activated carbon in a gravity settler. For a time period of 33 min. the underflow concentration reaches 6 times that of the influent concentration. By adding coagulation agents such as polymer or alum, it is expected to increase the settlability. However, chemical conditioning as such may release the adsorbed Cd(II) species from the activated carbon surface, thus defeating the original purpose of carbon treatment. In the laboratory, it is possible to separate the powdered activated carbon by centrifugation at 15000 g for

15 min with good solid recovery. However, the extreme fineness of the powdered carbon particles always renders the centrifugal operation ineffective.

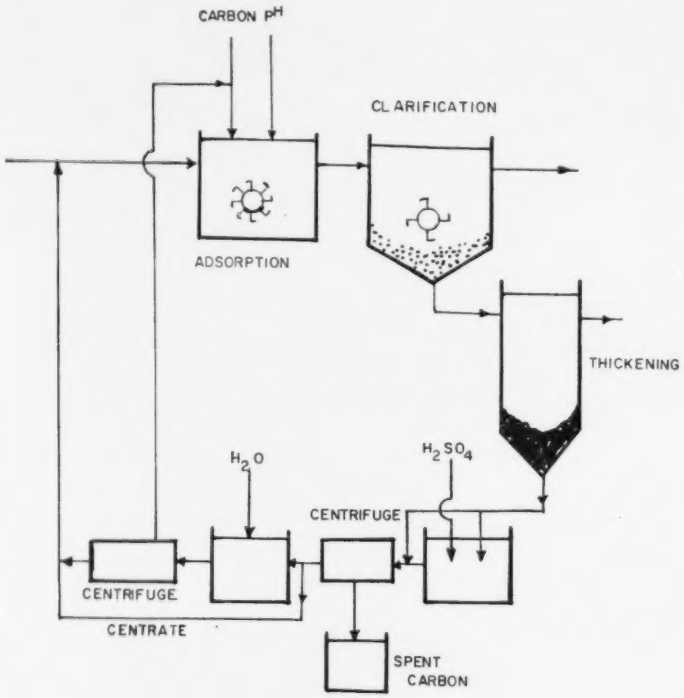


Figure 45. Schematic diagram of a CMFR activated carbon adsorption treatment system (with carbon regeneration).

The major capital cost items are installation of reaction tanks, carbon separation system and land aquisition. Operationally, the make-up of activated carbon constitutes the major cost item. Figure 46 shows the estimated annual cost of the CMFR system at various flow rates. As expected, the annual capital cost (amortized) is relatively unimportant comparing with the annual operational and maintenance cost. Table B-1 gives the details of cost calculation.

Column Reactor (CR)

Column reactor is another possible treatment scheme. This is made possible with the activated carbon beads.

The major advantages of the column operation are easiness in regeneration and compactness in installation. At exhaustion, the influent is disconnected from the exhausted columns and switches to other active carbon reactors. The used carbon is then regenerated in the exhausted column with H_2SO_4 directly (Figure 47).

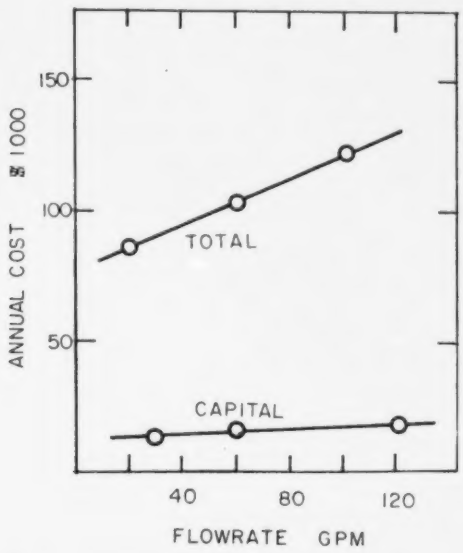


Figure 46. Estimated costs for a CMFR activated carbon adsorption system.

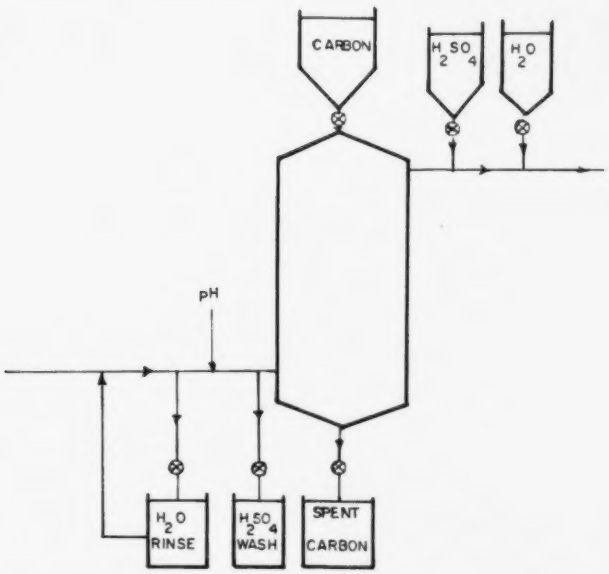


Figure 47. A schematic diagram of a CR activated carbon adsorption system (with carbon regeneration).

The spent carbon may be discarded without regeneration. However, the decision to regenerate or not is made entirely on the cost basis. The capital cost of an adsorption system is primarily a function of the volume of carbon in system and the type of configuration of contactor, e.g., single-stage, two-stage, etc., used. The economical analysis presented in this study is for single-stage contactor according to Zanitsch and Stenzel (62). The capital cost, CC, for low range flow rate (i.e., < 100 gpm) is a linear function of the carbon volume (V, in m^3) in system:

$$CC(\$1000) = 70 + 3V \tag{13}$$

When reactivation is performed on-site, additional capital investment is needed for the storage and handling of the used carbon. The capital cost for regeneration system is also a linear function of volume (V, in m^3) of carbon to be regenerated. The following relationship is derived from Zanitsch and Stenzel (62).

$$CC(\$1000) = 40 + 1.3V \tag{14}$$

The major operational cost consists of utilities, labor, monitoring, and chemicals. The cost of carbon beads (at \$0.6 ∿ \$0.8/lb) outweighs other chemical costs and is a major operational cost item. Therefore regardless of the additional investment cost, for regeneration systems, it is still worthwhile to regenerate the used carbon. The annual cost of the column reactor is shown in Figure 48. Table B-2 gives details of the economical estimation. The results show that the once-through approach is definitely undesirable. The results also indicate that a 30-day operation cycle and a 15-day operation cycle do not yield significant difference in total annual cost. Moreover, as always expected for wastewater flow, the capital cost only constitutes a small fraction of the total cost.

TREATMENT OF THE Cd-CN TYPE WASTEWATER

Since CN is extremely lethal and highly volatile at low pH (< 9.5), it is necessary to separate the cyanide ions from the wastewater prior to activated carbon treatment. Experimental results, however, do indicate that Cd(II) can be readily removed from wastewater that contains CN. Moreover, Huang and his associate found that activated carbon can also effectively remove CN from wastewater (43,50). Therefore, a simultaneous removal of Cd(II) and CN by activated carbon adsorption and concurrent collection of HCN gas produced in the system by lowering the pH value (for optimum adsorption), is also a possible treatment scheme. However, since the extent of Cd(II) adsorption is somewhat decreased in the presence of CN, it is desirable to remove CN from the wastewater prior to treatment by activated adsorption.

The separation of CN from wastewater is a simple operation. Cyanide can be destroyed by oxidation with Cl_2, O_3 or other oxidizing agents (63); CN can also be stripped from water under acidic condition, collected and

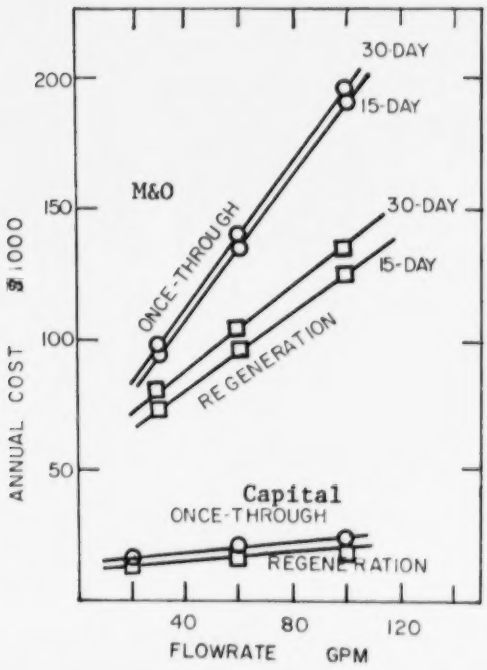


Figure 48. Estimated costs for CR activated carbon adsorption system.

concentrated in an alkaline solution. The results showed in Figure 49 indicate that air stripping is effective in CN removal. By adjusting the pH of the wastewater to *ca* 5.5, it is possible to remove the CN by air stripping and collecting the HCN gas in an alkaline solution (10^{-1} M NaOH) in a time period of 4 hours and at an air flow rate of 2 ℓ/min.

Comparison With Other Processes

Many methods have been suggested for the treatment of metal finishing industrial wastewaters (18). In this present study, the economical feature of activated carbon processes was compared with two precipitation processes, namely alkaline and insoluble sulfide, and an ion exchange process.

In a typical alkaline precipitation process, lime or caustic agent is used to neutralize the excess acid and to form $Cd(OH)_2(s)$ precipitate (Figure 50). The $Cd(OH)_2(s)$ precipitate is first separated by clarification then stored in a thickener for further improvement in sludge solid content. The $Cd(OH)_2(s)$ slurries may be disposed as they are or dewatered further (filter press, etc.) before ultimate disposal. The effluents from the clarifier and the thickener after sand filtration can be discharged to municipal sewer system; whereas the filtrate from the sludge filter is returned to the neutralization tank.

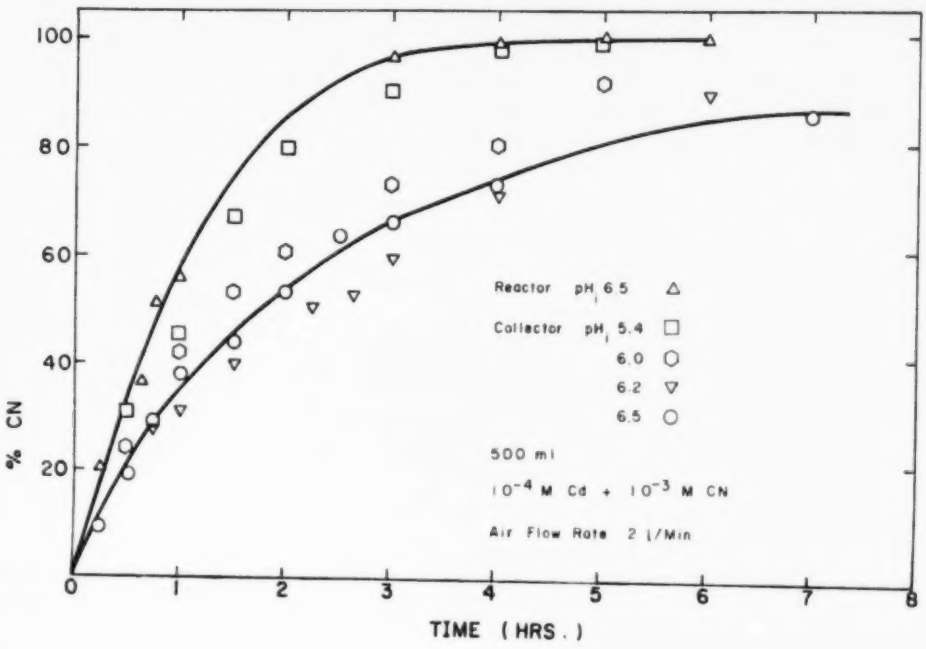


Figure 49. The kinetics of CN stripping by air.

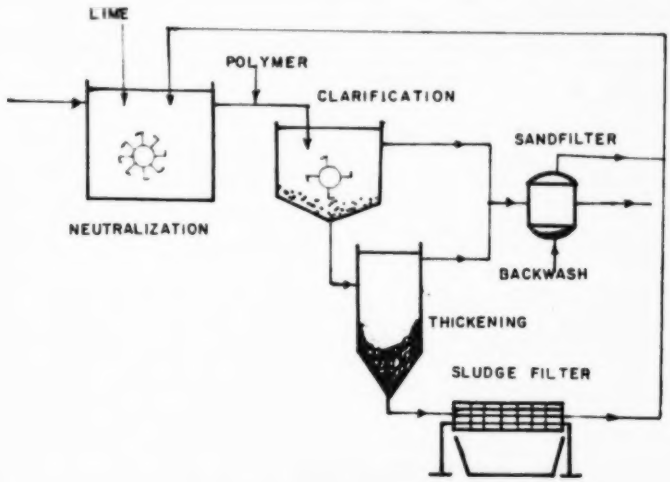


Figure 50. A schematic diagram of alkaline-neutralization-precipitation process (with polishing).

The sulfide precipitation system is a commercialized process, Sulfex^{TM} using insoluble FeS(s). A typical system uses two-stage neutralization. Ferrous sulfide and polymer are added simultaneously in a third precipitation tank where the solids CdS(s) and $Fe(OH)_2$(s) are formed. The metal precipitates, e.g., CdS(s) and $Fe(OH)_2$(s) are first separated by clarification. In the Sulfex^{TM} system, the sludge produced in the clarifier is treated directly by sludge filter without thickening (Figure 51).

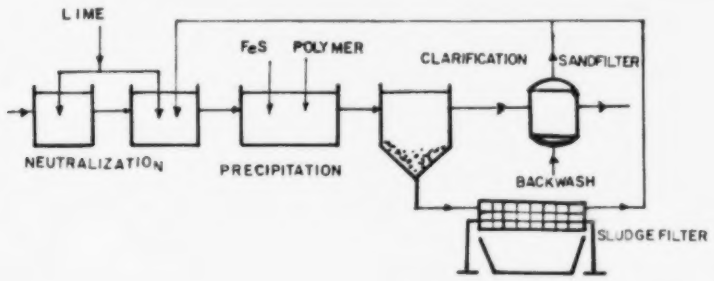


Figure 51. A typical insoluble sulfide precipitation treatment scheme (Sulfex^{TM}).

The operational set-up for ion exchange process is essentially the same as the activated carbon adsorption process except that cation exchange resin is used instead of activated carbon beads.

The total annual cost for the alkaline-neutralization-precipitation process was estimated according to the 1979 EPA report (64). The total annual cost for the insoluble sulfide precipitation was taken from the 1980 EPA report (65). The total annual cost for the ion exchange process was estimated based on the method suggested by Zanitscht and Stenzel (62). The results of estimated total annual cost for all processes compared are shown in Figure 52.

From the results shown in Figure 52, it is seen that the activated carbon adsorption process is economically promising comparing with the Sulfex^{TM} process and the ion exchange process. At a flow rate of 100 gpm, for example, the unit cost is \$6.9, \$3.7 and \$2.8-2.9 per 1000 gallons respectively for the Sulfex^{TM}, the ion exchange process and the activated carbon adsorption process. The results also show that the cost of the alkaline precipitation process is definitely less than the activated carbon adsorption process at \$1.9/1000 gallons. However, it must be mentioned that the estimated cost for the alkaline precipitation process is based on the assumption that the sludge treatment and disposal is operable. Any difficulty encountered during solid separation will significantly raise the treatment cost of this process. Incidently, Rouse (66) reported a unit cost of \$2.5-\$5.00 per 1000 gallons. Furthermore, whenever the Cd(II) concentration drops below *ca* 1 ppm (10^{-5} M), the precipitation reaction usually proceeds very slowly with the formation of extremely fine precipitate rendering solid-liquid separation difficult if

not impossible. Under such circumstances, it is not possible to assure the effluent quality.

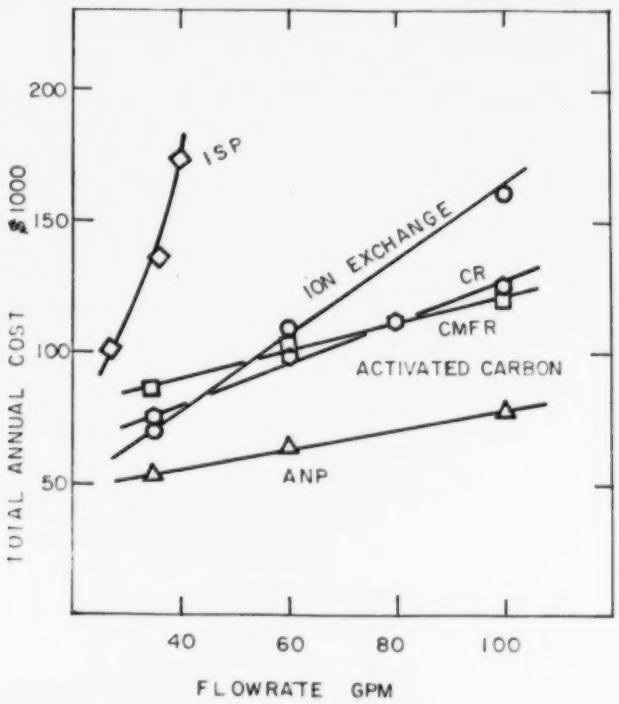


Figure 52. Estimated total annual cost for various cadmium treatment processes.

It is important to note that ion exchange process is more expensive than the activated carbon adsorption process. This is attributed to the cost of ion exchange resin. While no commercial activated carbon beads are yet available for comparison, based on the information obtained in this laboratory, the unit cost of carbon beads will be a few cents more than the powdered activated carbon with labor being the dominating cost item. Details of the economical considerations for all treatment schemes are shown in Appendix B.

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APPENDIX A

FORMULATION FOR EQUILIBRIUM CALCULATIONS
OF AQUEOUS CD(II) CHEMISTRY

Metal Speciation

The extent of coordination (or complex formation), like any other chemical reaction is dependent on a favorable free energy change. Cadmium (II), in the aqueous phase can take on many chemical forms depending on the presence of ligands, pH, and the concentrations of all soluble species. The distribution of the metal among respective ligands is governed by equilibrium calculations based on thermodynamic stability constants. A general expression for complexation between a metal, M^{+2}, and a ligand, L^{n-}, is:

$$M^{m+} + xL^{n-} = ML_x^{m-xn} \tag{A-1}$$

The stability constant at infinite dilution for the reaction is defined as:

$$\beta_x = \frac{\{ML^{m-xn}\}}{\{M^{m+}\}\{L^{n-x}\}} \tag{A-2}$$

where { } indicates the activities of the dissolved species. However, since solutions are dilute and at constant ionic strength, it is convenient to substitute concentrations for activities.

$$\beta_x = \frac{[ML^{m-xn}]}{[M^{m+}][L^{n-x}]} \tag{A-3}$$

where [ ] designates solute concentrations.

The total metal concentration can be expressed as the total of its present forms;

$$M_T = [M^{m+}] + \Sigma[ML_x^{n-xn}] \tag{A-4}$$

substituting equation (A-3) into equation (A-4) yields;

$$M_T = [M^{m+}] + \Sigma\ \beta_m[M^{m+}][L^{n-}]^x \tag{A-5}$$

A correction of the stability constants is desirable to agree with the ionic medium used with the experimental solutions.

Ligands in aqueous solution predominantly behave as Bronsted bases. Consequently, the concentration of the metal binding ligand L^{n-}, and the metal speciation is dependent on the solution pH. Analogous expressions for the total ligand concentration can be formulated.

$$H^+ + H_iL^{i-n} = H_{i+1}L^{(i+1)-n} \tag{A-6}$$

$$\beta_{i+1} = \frac{[H_{i+1}L^{(i+1)-n}]}{[H^+][L^{i-n}]} \tag{A-7}$$

$$L_T = [L^{n-}] + \Sigma\ \beta_{i+1}[H^+][L^{i-n}]^{i+1} + \Sigma\ \beta_x[M^{m+}][L^{n-}]^x \tag{A-8}$$

These equations allow for the calculation of the concentrations of the various metal species as a function of pH. Solutions to these equations can become difficult depending on the order of the resulting polynomial, and therefore require the use of the computer (60).

Metal Solubility

For a given solubility reaction,

$$M_nA_m\ (s) = nM^{m+} + mA^{n-} \tag{A-9}$$

the solubility product, K_{so}, is defined by;

$$K_{so} = [M^{m+}]^n[A^{n-}]^m \tag{A-10}$$

From the latter equation (A-10) it can be seen that the solubility of the metal salt is a function of the 'free' metal and ligand concentrations. Therefore, coordination with other species can result in a sizeable increase in metal solubility. The conditional solubility product concept, introduced by Scharzenbach and employed by Stumm and Morgan (34) can be used to quantify metal solubility occuring simultaneously with complex reactions. The conditional, solubility product P_s, is defined as;

$$P_s = M_T^n\ A_T^m = \frac{K_{so}}{\alpha_M^n\ \alpha_A^m} \tag{A-11}$$

where M_T and A_T are the total soluble metal and anion concentrations, respectively. The total anion concentration can be expressed as;

$$A_T = [A^{n-}] + \Sigma[H_{i+1}A^{(i+1)-n}] + \Sigma\ x\ [MA_x^{m-xn}] \tag{A-12}$$

The α values of equation (A-11) represent the fraction of the total metal or anion concentration which remains uncomplexed under a given set of conditions. The two α values can be expressed as;

$$\alpha_M = \frac{M^{m+}}{M_T} = (1 + \Sigma\ \beta_x [L^{n-}]^x)^{-1} \qquad \text{(A-13)}$$

$$\alpha_A = \frac{A^{n-}}{A_T} = (1 + \Sigma\ \beta_{i+1} [H^+][A^{n-}]^i + \Sigma\ x\ [M^{m+}][A^{n-}]^{x-1,-1} \qquad \text{(A-14)}$$

From equation (A-10), the total soluble metal that can coexist with the given solid phase can be determined as a function of the pH and the total ligand concentration.

$$M_T = \frac{K_{so}}{\alpha_M^n\ \alpha_A^m\ A_T} \qquad \text{(A-15)}$$

APPENDIX B

ECONOMICAL EVALUATION OF CD(II) TREATMENT SCHEMES

In the following analysis, the following conditions applied to all processes: 1. flow rate:100 gpm; 2. influent Cd(II) concentration:10^{-4} M (or 11.4 ppm; 2.48 x 10^{-5} lb/ℓ; 9.39 x 10^{-3} lb/min); 3. effluent Cd(II) concentration:10^{-6} M (0.11 ppm); and 4. annual operation period:300 days. The cost items that were subject to economical evaluation include chemicals, utilities, labor, maintenance, monitoring and overhead. The unit cost for chemicals pertinent to this analysis was adopted from the EPA reports (63,64) and are listed as follows: carbon beads @ \$0.70/lb; powdered carbon @ \$0.60/lb; cation exchange resin @ \$9.01/lb; H_2SO_4 @ \$0.05/lb; NaOH @ \$0.08/lb; $Ca(OH)_2$ @ \$0.02/lb; polymers @ \$1.4/lb; FeS @ \$0.4/lb. The cost of utilities was estimated at 3-5% of capital cost and maintenance cost was assumed at 6-8% of capital cost. Costs of labor and monitoring and overhead were estimated at 1 man-year each except the CMFP activated carbon adsorption process.

Activated Carbon Adsorption Process

CMFR Mode

1. Total Cd(II) removed: 0.99 x 10^{-4} x 9.39 x 10^{-3} = 9.29 x 10^{-3} (lb/min) or 4015 (lb/yr) @ 300 days/yr or 13.4 lb/day

2. Total carbon needed: [@ 100% utilization and 300 μM/gm adsorption capacity or 3.37 x 10^{-2} (lb Cd/lb carbon] 4015 (lb/yr)/3.37 x 10^{-2} = 119,069 lb/yr or 0.3 lb/min

3. Adsorption tank:
   retention tank: 15 min.
   volume: 100 x 15 = 1500 gallons
   pH: 7
   carbon dose: 0.3 lb/100 gal. = 372 mg/ℓ or 0.03% solid

4. Clarification tank:
   retention time: 33 min.
   underflow concentration: 0.16% solids
   underflow rate: 17 gpm
   overflow rate: 83 gpm

5. Thickener:
   retention time: 60 min.
   underflow concentration: 5% solid
   underflow rate: 0.7 gpm
   overflow rate: 16.3 gpm

6. Regeneration tank no. 1: ($1\ M\ H_2SO_4$ washing) — retention time: 2 hrs.; influent flow rate: 0.63 gpm; acid rate: 6.4 ℓ/min.

7. Regeneration tank no. 2: (H_2O rinsing) — retention time: 6 hrs.; influent: 0.63 gpm

TABLE B-1. Estimated Costs ($1000) for CMFR Activated Carbon Adsorption System*

Flow Rate (gpm)	100	60	30
Capital Costs+			
Adsorption tank	26.0	24.0	20.0
Clarifier	50.0	48.0	40.0
Pumping	6.0	5.0	4.0
Thickener	10.0	8.0	6.0
Storage tanks (for carbon, H_2SO_4, H_2O, and CaO)	10.0	8.0	6.0
Centrifuge	8.0	8.0	8.0
Land	4.0	3.0	2.0
Subtotal	114.0	104.0	86.0
Operational & Maintenance Costs			
Chemicals	2.0	1.2	0.6
Carbons	39.0	23.5	11.9
Utilities¶	5.7	5.2	4.3
Labor±	24.0	24.0	24.0
Maintenance and overhead†	9.1	8.3	6.9
Monitoring±	24.0	24.0	24.0
Amortization△	18.2	16.6	13.8
Total Annual Cost ($1000)	122.0	102.8	85.5
Unit Cost ($/1000 gallons)	2.82	3.97	6.60

*Mid-1979 dollars; 300 operation days per year.
+Estimated from reference (64).
¶@ 5% of capital cost.
±1.5 man-year @ $16,000/man-year.
†@ 8% of capital cost.
△@ 10% interest rate for 10 years or a capital recovery factor (CRF) of 0.16.

Column Reactor (CR) Mode

1. Total carbon needed (@ 100% column exhaustion): 13.41 (lb/day) x 300 (day/yr)/3.37 x 10^{-2} (lb Cd/lb Carbon) = 119,069 (lb/yr)

2. Total carbon needed at the breakthrough point (@ 64% exhaustion): annual carbon = 119,069 (lb/yr)/0.64 = 186,045 (lb/yr)

3. Total carbon needed if column is to be regenerated for four cycles at 64%, 57%, 48%, and 37% column capacity at exhaustion point during succeeding operations: (0.64 + 0.57 + 0.48 + 0.37)x = 119,069 (lb/yr) or x = 119,069/2.06 = 57,803 (lb/yr).

4. Volume of carbon based on laboratory column (0.088 lb carbon beads packed in 109 cm^3 column):

   i. for 30 days cycle duration

   $$V_1 = \frac{186,045}{12} \times \frac{109}{0.088} = 19.2\ (m^3)$$

   ii. for 15 days cycle duration

   $$V = \frac{186,045}{74} \times \frac{109}{0.088} = 8.6\ (m^3)$$

5. Exhaustion rate @ 10% of column carbon:

   i. for 30 days cycle duration

   $$\text{carbon exhausted} = 0.1 \times \frac{186,045}{12 \times 30} = 52\ (\text{lb/day})$$

   ii. for 15 days cycle duration

   $$\text{carbon exhausted} = 0.1 \times \frac{186,045}{24 \times 30} = 26\ (\text{lb/day})$$

TABLE B-2. Estimated Costs for CR Activated Carbon Adsorption System*

Flow Rate (gpm)	100				60				30			
Operational Approach	Throwaway		On-Site Reactivation		Throwaway		On-Site Reactivation		Throwaway		On-Site Reactivation	
Capital Costs												
Adsorption system[+]	130.0[+]	117.0[¶]	152.0[+]	117.0[¶]	126.0[+]	101.8[¶]	126.0[+]	101.8[¶]	103.0[+]	93.3[¶]	103.0[+]	93.3[¶]
Inventory/Reactivation System[Δ]	--	--	4.7	3.6	--	--	3.9	3.2	--	--	3.2	2.9
Subtotal	130.0	117.0	156.7	120.6	126.0	101.8	129.9	105.0	103.0	93.3	106.2	96.2
Operation & Maintenance Costs												
Chemicals:												
NaOH[δ]	2.0	2.0	2.0	2.0	1.2	1.2	1.2	1.2	0.6	0.6	0.6	0.6
H_2SO_4[ξ]	--	--	17.0	17.0	--	--	10.2	10.2	--	--	5.1	5.1
Carbon[→]	125.0	125.0	39.0	39.0	75.6	75.6	23.5	23.5	37.8	37.8	11.9	11.9
Utilities[√]	4.6	4.6	7.8	6.0	3.8	3.1	6.5	5.3	3.1	2.8	5.3	4.8
Labor[▽]	16.0	16.0	16.0	16.0	16.0	16.0	16.0	16.0	16.0	16.0	16.0	16.0
Maintenance[ϕ]	9.0	9.0	12.5	9.6	7.6	6.1	10.4	8.4	6.2	5.6	8.5	7.7
Monitoring and overhead[▽]	16.0	16.0	16.0	16.0	16.0	16.0	16.0	16.0	16.0	16.0	16.0	16.0
Amortization[‡]	24.3	18.7	25.1	19.3	20.2	16.3	20.3	16.8	16.5	14.9	17.0	15.4
Total Annual Cost ($1000)	196.9	191.3	135.4	124.9	140.4	134.3	104.6	97.4	96.2	93.7	80.4	73.5
Unit Cost $/1000 gallons	4.56	4.43	3.13	2.89	5.42	5.18	4.04	3.76	7.42	7.23	6.20	5.67

*In Mid-1979 dollars
[+]30-days cycle duration
[¶]15-days cycle duration
[Δ]Estimated with equation (12)
[+]Estimated with equation (13)

[Δ]Adjusting pH from 4 to 7 and @ $0.04/lb.
[δ]@ $0.05/lb.
[→]@ $0.70/lb.
[‡]@ 10% for 10 years or CRF of 0.16

[√]@ 3% and 5% respectively for throwaway and on-site reactivation
[▽]@ 1 man-year
[ϕ]@ 6% and 8% of capital costs respectively for throwaway and on-site reactivation

Alkaline-Neutralization-Precipitation Process

1. Neutralization precipitation tank

   Retention time: 10 to 30 min.
   Solid concentration-effluent: 0.01%
   Cost estimated from Fig. 4 of reference (64)

2. Clarifier

   Retention time: 4 to 6 hours
   Underflow concentration: 0.1%
   Underflow rate:
   Cost estimated from Fig. 5 of reference (64)

3. Sludge thickener and storage

   Retention time: 7 days
   Sludge volume: 731 gallons
   Solid concentration: 20%
   Cost estimated from Fig. 6 of reference (64)

4. Sludge filter

   Sludge produced: 73.1 gallons
   Cost estimated from Fig. 7 of reference (64)

Insoluble Sulfide Precipitation Process (Sulfex™)

Design details were those reported by the EPA (65). The capital costs at 15, 35 and 40 gpm respectively, were directly taken from the EPA's pilot plant studies (65). The costs for sludge disposal and chemicals at 40 gpm capacity were also taken directly from this same EPA report. The other operational and maintenance costs were estimated as above. Appendix B-4 shows the details of cost analyses for a typical ISP process.

TABLE B-3. Estimated Costs ($1000) for Alkaline-Neutralization-Precipitation Process*

Flow Rate (gpm)	100	60	30
Capital Costs			
Neutralization[+]	30.2	27.0	24.8
Clarifier[¶]	25.9	18.4	11.9
Thickener[+]	6.0	6.0	6.0
Sludge filter[+]	16.5	15.0	7.5
Subtotal	78.6	66.4	50.2
Operation & Maintenance Costs			
Chemicals:			
Polymer[¶]	6.0	3.6	1.8
Lime	4.0	2.4	1.2
Utilities[±]	3.9	3.3	2.5
Labor[‡]	16.0	16.0	16.0
Maintenance[Δ]	6.3	5.3	4.0
Monitoring and overhead[‡]	16.0	16.0	16.0
Sludge disposal[§]	13.2	7.9	3.9
Amortization[∞]	12.6	10.6	8.0
Total Annual Cost ($1000)	78.0	65.1	53.4
Unit Cost ($/1000 gallons)	1.81	2.51	4.12

*In Mid-1979 dollars
[+]Estimated from reference (64).
[¶]@ $1.4/lb.
[±]@ 5% capital cost
[‡]@ 1 man-year
[Δ]@ 8% capital cost
[§]@ $0.2/gallons and solid content 20%
[∞]@ 10% interest rate and 10 year or CRF 0.16

TABLE B-4. Estimated Costs for Insoluble Sulfide Precipitation Process (Sulfex™)*

Flow Rate (gpm)	15	35	40	60	100
Capital Costs					
Reactors and Installation	169+	195+	303+	401	420
Operation & Maintenance Costs					
Chemicals¶	16.4	38.3	43.8+	65.7	109.5
Utilities±	8.5	9.7	15.2	20.0	21.0
Labor†	16.0	16.0	16.0	16.0	16.0
Maintenance△	13.5	15.6	24.2	32.1	33.6
Monitoring and overhead†	16.0	16.0	16.0	16.0	16.0
Sludge Disposal§	4.1	9.5	10.8+	16.2	27.0
Amortization∞	27.0	31.2	48.5	64.2	67.2
Total Annual Cost ($1000)	101.5	136.3	174.5	230.2	290.3
Unit Cost ($/1000 gallons)	15.66	9.01	10.10	8.88	6.72

*In Mid-1979 dollars
+Estimated from reference (64).
¶Estimated from +.
±@ 5% of capital cost.
†@ 1 man year
△@ 8% of capital cost.
§@$0.19/gallons and solid content 30%
∞@ 10% interest rate and 10 years or CRF of 0.16

Ion Exchange Process

1. Total cadmium removed: $0.99 \times 9.39 \times 10^{-3} \times 2$ (eq/M x 378.5 (ℓ/min) x 60(min/hr) x 24(hr/day) x 300(day/yr) = 3.24×10^{4} (eq/yr)

2. Total dry weight of ion exchanger needed @ 1.9×10^{-3} eq/m^3 resin or 4.6×10^{-3} eq/gm dry resin as cation ion exchange capacity: 3.24×10^{4} (eq/yr)/4.6×10^{-3} (eq/gm) = 7.04×10^{6} (gm/yr) = 10,057 (kg/yr) (by weight) (eq/m^3) or 3.24×10^{4} (eq/yr) /1.9×10^{-3} (eq/m^3) = 1.7×10^{7} (m^3/yr) = 17 (m^3/yr) (by volume)

3. Assume 70% utilization at breakthrough: total volume of resins needed = 17/0.7 = 24 (m^3/yr)

TABLE B-5. Estimated Cost for Ion Exchange Process*

Flow Rate (gpm)	100	60	30
Capital Costs			
Exchange system+	142.0	85.0	42.6
Resin¶	201.1	120.7	60.3
Operation & Maintenance Costs			
Resin±	10.0	6.0	3.0
Utilities†	17.2	10.3	5.1
Labor△	16.0	16.0	16.0
Maintenance§	27.4	16.5	8.2
Monitoring and overhead△	16.0	16.0	16.0
Amortization∞	75.0	45.0	22.5
Total Annual Cost ($1000)	161.6	109.8	70.8
Unit Cost ($/1000 gallons)	5.46	4.24	3.74

*In Mid-1979 dollars
+Estimated by equation (12)
¶@ $9.09/lb or $20.0/kg
±Estimated 5% exhaustion
†@ 5% capital cost
△@ 1 man-year
§ 8% capital cost
∞@ 10% interest rate and 10 years and 5 years, respectively, for the exchange system and the resin (or CRF of 0.16 and 0.26 respectively).